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# NOVEL REGENERATION METHOD FOR ION EXCHANGE SYSTEMS

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FINAL REPORT

# NOVEL REGENERATION METHOD FOR ION EXCHANGE SYSTEMS

USPHS CONTRACT PH 86-63-120

by
I. R. Higgins

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U S Department of Commerce
Springfield VA 22151

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JAN 25 1965

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## 1.0 INTRODUCTION

The Advance Waste Treatment Research Program of the Public Health Service has two ultimate goals: To alieviate the Nation's growing water pollution problem, and to renovate waste for direct and deliberate re-use. To accomplish these objectives will require the use of waste water treatment methods, capable of removing a greater variety and amount of contaminants at a lower cost than present treatment methods.

One general category of contaminants is the inorganic ionic materials. One method of removing these materials is by ion exchange. Ion exchange is recognized as a highly effective method for removing anions and cations from water. The objectionable feature of conventional ion exchange, however, has been that relatively high priced chemical regenerants must be purchased, and dilute regenerant wastes must be disposed of.

The objective of this development program is to demonstrate a low-cost ion exchange system employing chemicals that can be re-used, and yielding final wastes in volumes that are practical for ultimate disposal.

The common cations in water are calcium, magnesium, sodium, and potassium which might be represented by "M". The common anions are bicarbonate, chloride, sulfate, phosphate, nitrate, and silica which might be represented by "A". The common ion exchange materials (resins) are divided into two groups; those that sorb or exchange cations, and those that sorb or exchange anions. The cation exchange steps of interest are as follows with "R" symbolizing the ion exchange material:

1. Cation Exchange Loading or Exhaustion:

$$Ma+ HR \longrightarrow MR + HA$$

2. Cation Exchange Regeneration:

$$MR + HNO_3 \longrightarrow HR + MNO_3$$

3. Anion Exchange Loading or Exhaustion:

$$HA + R \longrightarrow R\text{-}HA \qquad \text{(weak-base)}$$

$$HA + R\,OH \longrightarrow RA + H_2O \quad \text{(strong-base)}$$

4. Anion Exchange Regeneration:

$$R\text{-}A + NaOH \longrightarrow ROH + NaR \text{ (strong-base)}$$

There are several potentially attractive systems for recovering and recycling the acid used to regenerate the cation exchange resin; the choice for this study is a nitric acid system. The reasons for using nitric acid are: (1) it is volatile, (2) it is compatible with stainless steel, (3) all nitrate salts are highly soluble, (4) it is relatively low cost, and (5) it is a highly ionized or a strong acid.

The key step in the flowsheet is the thermal decomposition of the nitrate salts to yield alkali and nitric acid for reuse. If the efficiency of this decomposition is reasonably high the heat cost will be considerably less than the chemical regenerants consumed in the usual demineralization system. There is an extensive background of information supporting the feasibility of this technique (1, 2, 3, 4, 5, and 6). The emphasis of this study is laboratory calcination (decomposition) work.

The basic economics for this system rests on the degree of success in generating usable caustic and acid from the neutral nitrate salts of the common alkali and alkaline-earth ions. Since some of the hydroxides are insoluble, full utilization can be obtained only by using weak-base anion exchange resin for anion removal, which can be regenerated with ammonia. The recycle of ammonia, by reacting lime and/or other hydroxides with the ammonium salts, is a standard unit operation.

After determining reasonable yield of regenerants from this calcination step, there are other contributory efficiency factors that are not standard with conventional fixed-bed ion exchange practice. By using a continuous ion exchange contactor, such as the Chem-Seps continuous, countercurrent contactor, throughput rates (gallons per minute per square foot of resin bed cross-section) five to ten times greater than in fixed-bed practice can be attained. This is reflected in a corresponding reduction in equipment size.

Voluminous rinses and dilute regenerant wastes are another characteristic of fixed-bed ion exchange. Again a contribution of continuous counter-current ion exchange is the capability to deliver compact waste streams. This is important since it is anticipated that these waste concentrates will be injected in or transported to permanent disposal areas, which is another section in the Advanced Waste Treatment Program.[1]

The purpose of this study is to outline and demonstrate an ion exchange water treatment system made low cost through a system of recovering and re-using regenerants. The need of this study is to prove that nitrate salts can be conveniently dissociated into acid and base useful for regeneration of ion exchange resins. The scope of this study covers laboratory scale steam calcination studies of nitrate salts, and continuous ion exchange runs to show economics in regenerant use and minimum dilution inherent in a continuous counter-current flow system.

## 2.0 SUMMARY

Description - This study has generally proved the technical feasibility and economic practicability of the proposed flowsheet, Figure #1, described in Section 3. It is an ion exchange process for removal of inorganic dissolved solids from raw water. Further it is a system for overcoming the economic disadvantage of ion exchange, i.e. the consumption of expensive chemical regenerants, by a unique recovery method. The basic steps of the flowsheet are:

(1) Removal of cations (principally sodium, potassium, calcium, magnesium and ammonium) by ion exchange using strong acid-type resin.

(2) Removal of bulk bicarbonate in a decarbonator to reduce the load on the anion exchange removal steps.

(3) Removal of strong acids (chloride, sulfate, nitrate and phosphate anions) by ion exchange using weak base-type resin to facilitate regeneration with weak alkali-ammonia.

(4) Removal of weak acids (silica and trace bicarbonate) by ion exchange using a strong base-type resin polishing operation.

(5) The regeneration of the cation resin with nitric acid. The decomposition of the nitrate salts from the regenerant effluent to produce nitric acid for reuse and alkali for ammonia recovery (weak base resin regenerant) and for regeneration of strong base polisher.

Economics - The economic impact of this flowsheet is seen from the analysis of the operating and amortization costs for a ten million gallon per day plant treating water with 280 ppm cations (683 ppm as $CaCO_3$).

| | |
|---|---|
| Operating Cost for 10-Million GPD Plant (Section 7.2) | 6.4¢/1000 gallons |
| Ultimate Disposal (Injection-7000 ft, 900 psi) | 0.5¢/1000 gallons |
| Amortization Cost for 10-Million GPD Plant (Section 7.1) | 4.9¢/1000 gallons |

Followup Program - Certain of the test results lack the technical rigor and conclusiveness hoped for from this study; the primary reason was the inability to develop and build equipment of sufficient size and with appropriate control within the budget of this project.

It is proposed in Section 8.0 that this study be continued toward the objective of large-scale industrial and municipal installations in two phases:

1. Pilot plant demonstration with prototype equipment to perfect equipment design and flowsheet conditions

2. Commercial scale installation (several million gallons per day) to demonstrate the economics.

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2.0 (continued)

Technology - The key to the technical practicability of the flowsheet and thus the concentration of the development effort was to demonstrate high yield regeneration of acid and alkali from the decomposition of alkali and alkaline earth nitrate salts. Individual studies were made in a small laboratory calciner handling 5 to 10 grams of calcium nitrate, sodium nitrate, magnesium nitrate and potassium nitrate. Yields of acid were as high as 100% from calcium and magnesium nitrate at 500°C to 600°C. Yields from sodium and potassium were 50% to 80% at temperatures close to 600°C.

In these small scale batch tests it could not be ascertained whether the relatively low yields for the sodium and potassium nitrate were the result of incomplete reaction or small losses. Residual nitrates were low with every indication that decomposition was complete. The surface tension of the residual product was so low that it spread over the entire reactor rather than being retained in the sample boat (which is the reason for thinking small losses could have occured and erroneously shown up as low yields). At times up to 5% of the sodium was found in the condensate indicating some volatility. The acid product appeared to be all nitrate with little or no reducing effect with permanganate, which indicated no nitrite.

Larger scale tests were run continuously in a 6 1/4" diameter calciner with a mixture of the above mentioned nitrate salts. The runs were made at the decomposition temperatures determined in the laboratory tests, yet the reactions were definitely incomplete. This could only be explained by too short a contact time. The laboratory experiments were run over two to four hour periods (because of the time required for warm up). Holdup time in the rotary calciner was estimated to be five to twenty minutes. These conditions rendered 80% to 85% decomposition of the alkaline earth nitrates; the alkali nitrates were two percent to five percent converted to hydroxide. There was good material balance between hydroxide formed and nitrate undecomposed. However, the method used for nitric acid recovery was inadequate. The off-gas was bubbled through a pot of flowing water and nitric acid yields analyzed only one percent to two percent.

The residue product was a free-flowing low surface tension slurry. This was most encouraging because it was anticipated that it might be sticky and unmanageable. Some volatilization of sodium nitrate was observed. This pilot study lasted only two twenty-four hour days and proper analytical facilities were not available onsite. It was valuable preliminary information, but sufficient runs under varying conditions were not made to carry the study to final satisfactory completion.

Continuous cation exchange data applicable to this flowsheet are available from other Chem-Seps projects. A 100,000 gpd water softener was operated on a 24-hour day basis for six months on water from 650 to 880 ppm hardness. Flowrates ranged from 35 to 75 gpm/ft$^2$ of resin bed cross section. Hardness was reduced to 20-30 ppm (an amount of raw water was blended back to yield an 85 ppm water for municipal consumption). Salt consumption was 0-10% excess over stoichiometric. Ferrous iron was also removed to the same degree as hardness without an iron oxide resin fouling problem.[2]

2.0 (continued...)

In this contract ion exchange studies were made to check the efficiency of nitric acid regeneration of cation exchange resin, ammonia regeneration of weak-base anion exchange resin, and sodium hydroxide regeneration of strong-base anion exchange resin. Nitric acid stripping efficiency was comparable to that demonstrated for salt or better. Operating conditions of stoichiometric to 10% excess acid use with regenerant salt strength up to 4 M in nitrate can be maintained. Weak-base type resin completely sorbed the mineral acid products of cation exchange resin--hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid. Regeneration with weak hydroxide-ammonia-was absolutely stoichiometric. A twenty-five percent excess of sodium hydroxide was used for strong-base resin regeneration with indications that somewhat less would be adequate.

The weak base anion exchange system using ammonia as the regenerant is considered the most attractive procedure because its common salts are very soluble, and it can be volatilized from regenerant wastes by adding the caustic produced in the nitrate decomposition, the quantity of which is more than sufficient to yield 100% ammonia recovery. To demonstrate that the yield was high, lime was added to a mixture of ammonium salts equivalent to what would be expected from anion exchange regeneration. The results indicated that the yield of ammonia was close to 100%. Residue ammonium ion was less than 0.4%.

## 3.0 PROPOSED FLOWSHEET (See Figure 1)

The proposed flowsheet is designed for removal of ion exchangeable materials from secondary effluents. It is presumed that a carbon sorption of organics might precede and/or some may be exchangeable on porous anion exchange material.

The Advanced Waste Treatment Research Program has collected data for municipal secondary effluents (See Appendix 10.1). Since there is no typical analysis for the whole country, maximum values were selected for the flowsheet. The cations amount to 280 ppm as the individual cation or 683 ppm as $CaCO_3$. Adjustments may be made for various degrees of mineralization. The flowsheet is equally applicable to natural raw waters. It is noted that secondary effluent has about the same quantitative analysis as the raw water in a given locale (somewhat higher in ammonia, phosphate, sodium, chloride, and nitrate).

Many features of the proposed flowsheet have been worked out in considerable detail in studies not covered in this contract, but are included in this report because they are a vital part of the over-all story. This is primarily work with the continuous ion exchange contactor which has to do with throughput rates, regeneration efficiency, regenerant waste concentration, and engineering design features.

The emphasis in this contract is on calcination of the cation exchange regenerant waste and the flowsheet values indicated have in some instances been extrapolated and not fully attained at this stage of the development work. Work with the anion exchange resins has not been as extensive as compared to cation exchange. Decarbonation and ammonia recovery are considered standard unit operations.

Proposed ultimate disposal methods are spreading, transporting to the sea, desert, etc. or underground injection. The important point as far as this flowsheet is concerned is that the wastes are delivered in a compact form of high concentration so that ultimate disposal costs are not an ove whelming factor.

The flowsheet is set up on the basis of 5,000,000 GPD, which is considered an optimum size for a single continuous ion exchange contactor, at least at the present stage of engineering development (Chem-Seps is building a six-foot diameter water softener.) The following description of the flowsheet steps can be related to Figure 1 by following through the main water flow, the cation exchange regenerant, and the anion exchange regenerants:

1. Raw water with the specified composition is fed through the loading section of a continuous ion exchange contactor at a rate of 69 gpm/ft$^2$. Contact time of water and resin is about 20 seconds. From the 280 ppm of mixed cations a breakthrough of $<1$ ppm can be attained. The exit water is a mixture of acids of the anions present.

3.0 (continued...)

2. It is fortunate that bicarbonate is the predominant anion because a low-cost removal method, decarbonation, is available for its elimination. It would by folly to sorb the carbonate on anion exchange resin and pay for regenerants when it can be almost completely removed by aeration. The water leaving the cation exchange contactor comes off bubbling vigorously and the decarbonator completes the carbon dioxide removal. This special removal of bicarbonate reduces the need for 100% yield of caustic in calcination. (For the particular combination of contaminants shown in the flowsheet, there would be a 32% excess of caustic over what is required for anion exchange regeneration). The released carbon dioxide might end up a waste, or it could be used for recarbonation or compressed and sold as dry ice. For 5,000,000 gpd of water with 327 ppm $HCO_3$ there is a release of 9360 lbs. of carbon dioxide.

3. Water leaving the decarbonator contains the strong acids, HCl, $H_2SO_4$, $HNO_3$, $H_3PO_4$, and the weak acids, silica and about 5% of the bicarbonate as tailings. This water next passes through a continuous contactor similar to that used for cation exchange, but filled with weak-base anion exchange resin. This resin sorbs the strong acids and leaves only carbonate, silica, and any other trace weak acids that may be present. The weak-base resin is used because it can be regenerated stoichiometrically with a weak alkali such as ammonia and because full utilization can be made of alkali and alkaline earth hydroxide regenerants (from step 5 below).

4. The quantities of weak acids present at this point are relatively small and a fixed-bed polisher containing strong base resin is proposed. (The choice between continuous or fixed-bed is based on production rate and resin loading rate.) Only sodium or potassium hydroxides can be used for strong base resin regeneration; only small quantities are required equivalent to the amount of silica and bicarbonate tailings. A situation could exist with high bicarbonate and high ratio of soluble hydroxides where strong base resin could be used in the continuous contactor and eliminate need for the weak-base resin. This would eliminate the fixed bed follow-up column and make the ammonia recycle system unnecessary.

5. The nitrate regeneration cycle operates as follows: Nitric acid 4 M in concentration is chosen as the regenerant. A high concentration is used to take maximum advantage of the mass action effect of the H-ion and minimize regenerant dilution. Based on related work a 25% excess of nitric acid over stoichiometric is used. This excess is not an item of great consequence since all free acid is recovered in the recycle system.

3.0 (Continued...)

5. (continued...)

Thermal energy is required to decompose the nitrate salts and form acid and alkali. The quantity and cost of heat required to decompose the concentrated nitrate solution is a fraction of that required for distillation of the total volume of water, which is approximately 400 times greater. Heat utilization per unit volume is less efficient for recycling nitric acid and calcining nitrate salts than simply evaporating water, but is justified because much less heat is required for the smaller volume. The total heat requirement to remove all the water from 4 M nitrate solution (to dry nitrate salts) and to decompose these nitrate salts to their respective hydroxides, from treatment of 5,000,000 gpd of water of the specified mineral content, is 310,000,000 BTU. It is noted that most of the heat requirement is for water removal, not nitrate salt decomposition. Therefore, emphasis is placed on avoiding dilution of regenerant wastes, and reducing the water content to a minimum.

The runs have demonstrated that the hydroxide product, at calciner temperature, will be a free flowing, low surface tension liquid slurry.

The final design of the denitrating equipment has not been established at this stage of development. If a rotary calciner is used, it would be desirable to flash off water and free nitric acid in an evaporator. Nitrate salts are very soluble and compatible with stainless steel even when hot. Traces of chloride, sulfate, or fluoride, which could aggravate corrosion are not present because they are effectively separated in the cation exchange step. Nitric acid produced from the calcination may be somewhat lower in concentration than the desired 4 M and this would be fed to a rectifying column. High nitrate yields are required because there is no other make-up source. When discussing steam calcination of calcium, magnesium, sodium, and potassium nitrate to their respective hydroxides and nitric acid it should be made clear that this is a key step in the process, and all phases of the technology have not been developed fully (See Section 4.0). (Other work is being done on carbonic acid regeneration of cation exchange resin, but this is at an earlier stage of development.[3])

6. The weak-base continuous ion exchange unit is regenerated with ammonium hydroxide because in the case of this resin regeneration efficiency is high even with this weak hydroxide, and because all ammonium salts of interest are highly soluble. Alkali from the calciner is added to the ammonium salts in a closed reactor. If the heat of reaction proves insufficient, an external source may have to be added. The off-gas ammonia is sorbed in a scrubbing tower to render 4 M ammonium hydroxide to be reused.

3.0 (Continued...)

6. (continued..)

Ammonia removal before calcination is desirable in order to save both the ammonium and nitrate ions associated with ammonium nitrate. On calcination ammonium nitrate would be entirely lost as non-recoverable gases. If some of the alkali (10% of the total) is added to the concentrated neutral nitrate salt solution, the ammonia can be flashed off and saved, and the associated nitrate combines with the alkali or alkaline earth ions. This is new ammonia added to the system from the raw water in this flowsheet amounts to 940 pounds or about 17% of the total needed. This means ammonia recovery would have to be only 83% to yield enough to satisfy anion exchange regeneration demands.

As already mentioned, high caustic yield is not required because of the release of carbon dioxide reduces the anions to a point where there is an excess of caustic over that required.

7. An important feature of the Advance Waste Treatment Program relative to conventional water treatment practice is that the final wastes must be disposed of in a manner that will prevent re-entry into the biological environment. It is practical to deliver the contaminants in a 4 eq/l volume that will be a mixture of soluble and insoluble salts. The volume is 0.25% of the original feed water treated. More volume reduction may be desired, but boil down of a corrosive slurry is not attractive and direct handling of the anion exchange regenerant waste, after ammonia removal, is recommended.

## 4.0 CALCINATION STUDIES

### 4.1 Laboratory Studies

Background - Reference has already been made to the background of work done on the thermal decomposition of nitrate salts. (Reference 4 through 9). It would be fortunate if the common minerals in water were salts of the transition elements such as aluminum or iron. These salts decompose very easily to yield nitric acid and metal oxides.[4] The common minerals in water, however, are salts of sodium, potassium, calcium, and magnesium. The nitrate salts of these cations decompose with more difficulty.

Sodium nitrate is of special concern to the nuclear industry because it is a bulk component of radioactive wastes. The AEC has worked on the thermal decomposition of this salt in order to reduce volume and immobilize the fission products by elimination of the soluble nitrate ion. The recovery of nitric acid is incidental to them, but their work is of value in reference to equipment technology and characteristics of nitrate salt breakdown.

The main objective of this Advanced Waste Treatment study is to obtain high yields of acid and base by simple thermal decomposition. The decomposition of these nitrate salts could be enhanced by adding a reducing agent (Hanford AEC Laboratories have used sugar). Reducing agents were avoided in this work to prevent excessive formation of nitric oxide (NO) or possibly nitrogen ($N_2$). Previous data indicated that the presence of water vapor encouraged a hydrolysis reaction and/or provided vapor cooling that allowed nitric acid to vaporize without dissociation into nitrogen dioxide ($NO_2$), nitric oxide (NO) and water vapor. More work is necessary to measure the beneficial effect of water vapor.

Description of Bench-Scale Laboratory Runs - The laboratory calcination studies were made in a one-inch stainless steel pipe in an electric tube furnace. Samples of nitrate salts were placed in a stainless steel boat. A 0.2 hp steam generator provided wet steam which was pre-heated either by another electric tube furnace or gas fired coil. Off-gas was run through a condenser and the condensate collected. Thermocouples were installed to measure the temperature in the reaction zone, and the preheated steam. See Figure 2.

The method of operation was to introduce the stainless steel boat containing a weighed sample of nitrate salt in the center of the furnace. Superheated steam was passed over the sample to provide adequate water availability for the formation of nitric acid. The temperature was raised to various levels and cuts of the acid were collected from the end of the condenser and titrated. At the end of a run the calciner was thoroughly flushed for residual salts and alkali.

A determination of the relation between reaction rate and temperature was difficult to accomplish by this batchwise method because the furnace heated up slowly. The ultimate temperature could be controlled, but because of the slow rate of heating it was not precisely determined if there was a critical temperature above which the decomposition rate sharply increased.

4.1 (continued...)

Analytical Procedure - Analytical methods employed were as simple as possible for the main constituents: the condensate was titrated for acid and the residue for base. When sodium or potassium nitrates were used the calciner residue was dissolved in water and titrated for alkali. The residue did not remain in the sample boat and the furnace had to be completely flushed. From later studies it was decided that the molten hydroxides had a low surface tension and spread throughout the reactor, or had a high vapor pressure and boiled out of the hot zone.

When runs were made with calcium or magnesium nitrates the residue was dissolved in excess acid and back titrated. Flame photometric analyses were made for sodium and/or potassium, both in residue and condensates. Corresponding titrations were made for hardness (EDTA Eriochrome T) when using calcium or magnesium nitrates.

Positive analysis was made for nitrate using either, and sometimes both, the Brucine and Phenoldisulfonic methods. Doubts arose about the reliability of both these methods and analyses for nitrates were not always made. Toward the end of the studies an ion exchange method was used for nitrates. Residue hydroxide was fed to H-form cation exchange resin and the breakthrough sample titrated for acid.

Occasionally there was reason to believe that there were reduced nitrogen compounds in the condensate or off-gas scrubber and permanganate titrations were used. Gravimetric analysis was used on the pre-run using aluminum nitrate because the product gave every appearance of being alumina ($Al_2O_3$).

Discussion of Results - Results are shown in Tables I, II, III, and Figure 3. Certain conclusions can be drawn, although there is enough inconsistency in the data to raise several questions.

There seems to be no question, however, about the complete decomposition of the nitrate salt. The ease of decomposition of the various nitrate salts in descending order appears to be Mg, Ca, Na, then K. The sharp termination of acid evolution seems to indicate that nitrate removal is complete, see Figure 3. A consistent carry-over of some sodium and potassium into the condensate, with absence of calcium or magnesium, indicates some volatilization of the alkali hydroxides and/or nitrates. The results indicate that there is about a 100°C difference between the lower temperature limits of decomposition for the alkaline earths and the alkali nitrate salts (500° versus 600°C).

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4.1 (continued...)

Acid yields in some of the earlier runs were low, below 50%, but erratic. It was decided that this was partly due to leaks in the equipment. With more care later runs seemed to render higher yields. At first the nitric acid product was titrated with permanganate with expectation that nitrous acid ($HNO_2$) was present. Only slight reducing effect was noted so this test was abandoned. On one test non-condensible gas was collected ($N_2$), but there was considerable air in the steam supply so this was meaningless. At high temperature, nitric acid is known to break down to nitrogen dioxide and nitric oxide. Apparently there was sufficient air available in the system to re-oxidize the nitric oxide and sufficient water to re-form nitric acid. Because the samples were small, 100% yields and good material balances were difficult to obtain. More positive evidence that there were no losses of unabsorbed or unoxidized nitrogen gases would be desirable. The nature of the decomposition and the absence of nitrate as determined from nitrate analyses, however, would seem to offer satisfactory evidence as to the completeness of nitrate removal.

TABLE I

STEAM CALCINATION OF CALCIUM NITRATE TETRAHYDRATE

| Date | Nitrate Milliequivalents | | | Residue Milliequivalents | | | °C | Hrs. Run |
|---|---|---|---|---|---|---|---|---|
| | Input | $HNO_3$ (in condensate) | % Yield H | Ca | $NO_3$ | % Yield OH | Max. Temp. | Time |
| May 10 | 42.2 | 36.4 | 86% | -- | 1.16 | -- | 665 | 1.4 |
| May 13 | 42.2 | 9.65 | 22.8 | -- | 1.14 | -- | 540 | 1.3 |
| May 14 | 42.2 | 5.08 | 12.2 | 36.0 | 1.0 | 38.2 | 510 | 1.2 |
| May 15 | 16.9 | 14.6 | 86 | 15.0 | 0.6 | -- | 595 | 1.5 |
| May 16 | 16.9 | 14.2 | 84 | 24.8 | 1.7 | -- | 630 | 2.9 |
| May 17 | 423 | 197 | 46.5 | -- | 24 | -- | 600 | 7.3 |
| May 20 | 211 | 165 | 77.5 | -- | | | 645 | 3.0 |
| May 21 | 211 | 198 | 94.0 | | 0.94 | | 670 | 4.5 |
| May 22 | 211 | 183 | 86.5 | | | | 575 | 1.8 |
| Nov.18 | 42.2 | 43.8 | 104 | | | | 600 | 2.5 |
| Nov.19 | 42.2 | 43.6 | 103 | 36.7 | | 87.0 | 430 | 1.8 |

STEAM CALCINATION OF MAGNESIUM NITRATE HEXAHYDRATE

| | | | | Mg | | | | |
|---|---|---|---|---|---|---|---|---|
| Dec.6 | 78.0 | 95.9 | 123 | 76.0 | -- | 97% | 600 | 4.5 |

TABLE II

STEAM CALCINATION OF SODIUM NITRATE

| Date 1963 | Nitrate - Meq Input | Condensate | Residue | %Yield Cond. $HNO_3$ | Sodium - Meq Input | Residue | Conds. | OH yield% based on Input Na | Residue | °C Temp | Hr. Run Time |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5/23 | 58.6 | 68.7 | 1.8 | 117% | | | | 5.1% | | 535 | 1.1 |
| 5/24 | 58.5 | 35.0 | 3.8 | 59.5 | 58.5 | 21.7 | 4.0 | 48.0 | 133% | 650 | 3.5 |
| *28 | 58.6 | 27.4 | 3.2 | 46.6 | 58.5 | 27.4 | 25.2 | 27.2 | 60.0 | 580 | 3.2 |
| 29 | 58.6 | 20.8 | 2.9 | 35.5 | 58.6 | 29.0 | 18.2 | 40.5 | 82 | 650 | 6.2 |
| 7/25 | 58.5 | 30.5 | | 54.7 | 58.5 | | | 10.4 | | 245 | 3.0 |
| 7/26 | 58.5 | 18.4 | | 31.5 | 58.5 | | | (sample lost) | | 165 | 2.5 |
| 11/20 | 58.6 | 46.6 | | 79.5 | 58.6 | 31.0 | 1.8 | 54.6 | 107 | 640 | 5.7 |
| 12/11* | 118 | 53.1 | | 45.0 | 118 | 166 | 11.0 | 46.3 | 32.9 | 670 | 3.0 |

*Carbon dioxide mixed with steam to form $Na_2CO_3$

STEAM CALCINATION OF POTASSIUM NITRATE

| | | | | | Potassium-Meq | | based on K | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 5/8 | 49.5 | 150.5 | | 302 | 49.5 | | 30.5 | | 680 | 2.1 |
| 5/9 | 49.5 | 6.76 | 1.53 | 13.6 | 49.5 | | 6.0 | | 540 | 3.3 |
| 12/3 | 100 | 34.5 | | 34.5 | 100 | 61.6 | 55.2 | 89 | 620 | 4.8 |

TABLE III

STEAM CALCINATION OF MIXED NITRATE SALTS OF CALCIUM, SODIUM, POTASSIUM AND MAGNESIUM

$KNO_3$-3.8%, $NaNO_3$- 43.6%, $Ca(NO_3)_2$, $4H_2O$- 29.5%, $Mg(NO_3)_2$, $6H_2O$-23.1%

| Date | Nitrate Input | - Meq. Condensate | $HNO_3$ % Yield | Residue - Meq. Ca+Mg | Na | K | %OH Yield based on input | Meq. Condensate Ca+Mg | Na | K | °C max. Temp. | Hr. Run Time |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Jan 15 | 76.3 | 57.9 | 76% | 21.5 | 31 | 1.5 | 71% | | 7.0 | 0.1 | 700°C | 3.7 |
| Feb.24 | 76.3 | 57.8 | 75.5 | 50 | 16 | 2.3 | 110 | nil | 4.9 | 0.8 | 680°C | 2.2 |
| Feb.25 | 76.3 | 29.5 | 38.7 | | | | | | | | 510 | 3.4 |
| | | 52.6 | 69.0 | 110 | 27 | 4 | | | 2.5 | 0.9 | 740 | 6.1 |
| Mar.13 | 76.3 | 62.0 | 81 | 110 | 27 | 4 | | | 1.0 | 0.4 | 610 | 3.1 |

# FIGURE 2
# LABORATORY CALCINER

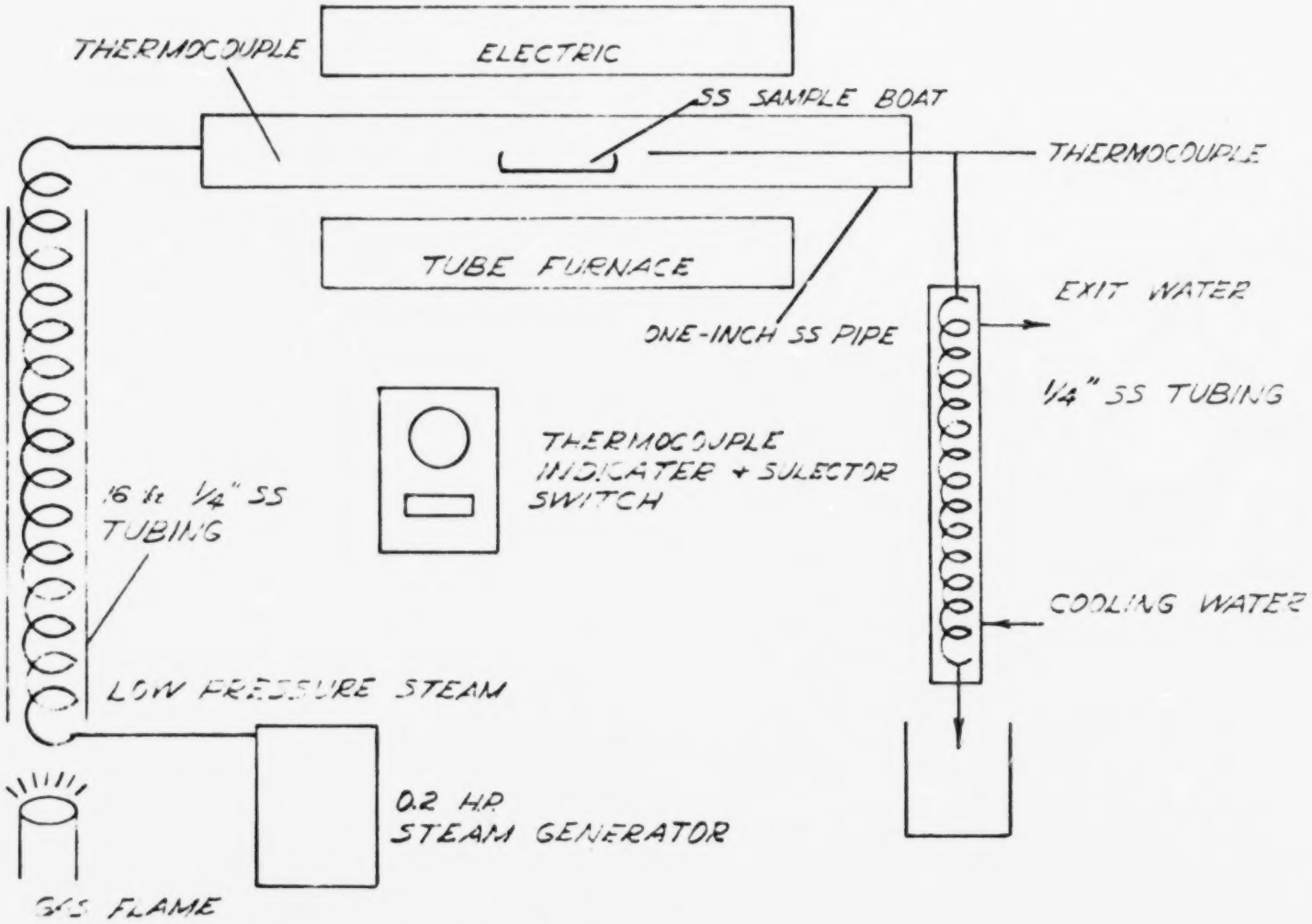
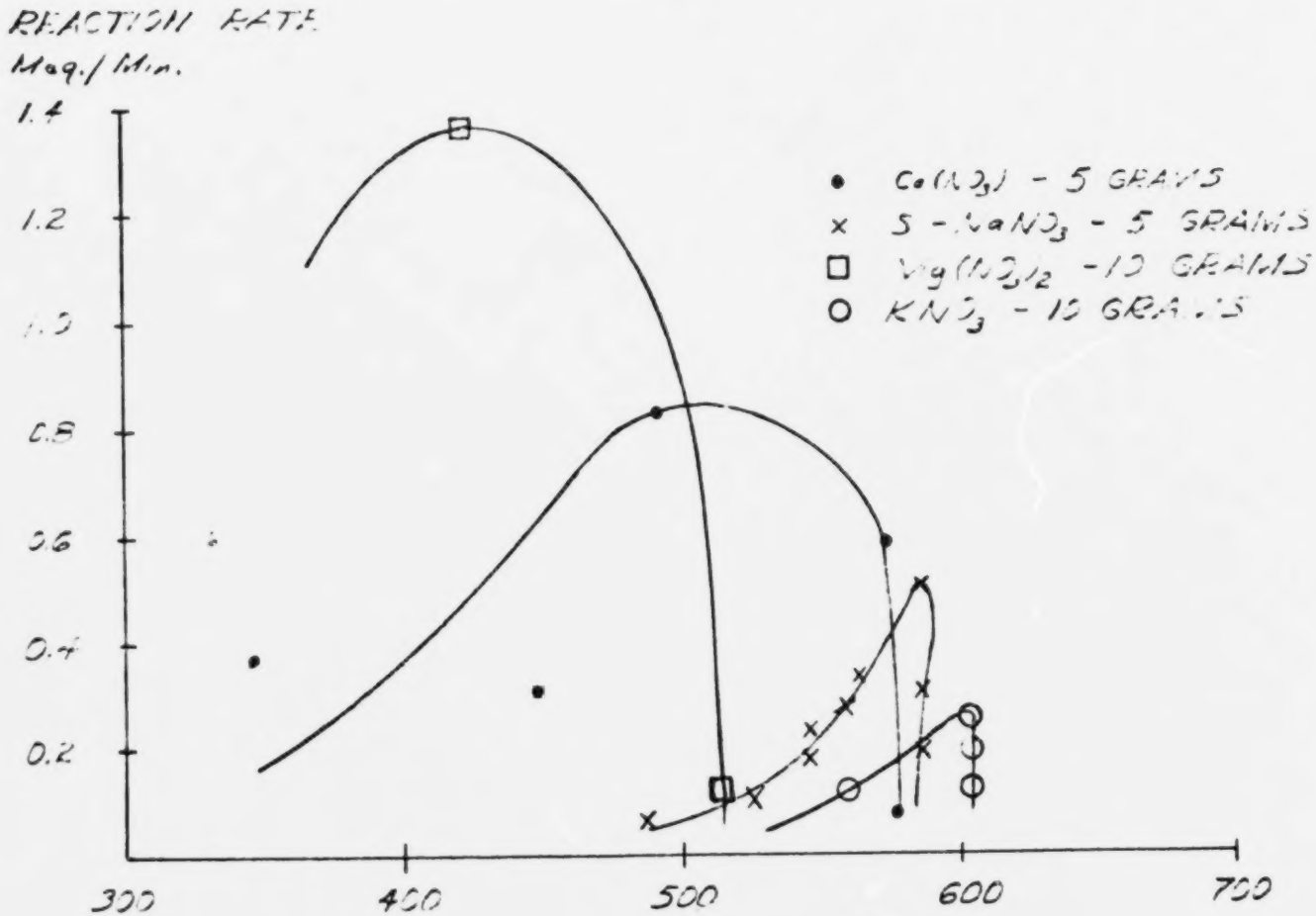


FIGURE 3

BATCHWISE STEAM CALCINATION OF NITRATE SALTS

DECOMPOSITION RATE VS. TEMPERATURE

EQUIPMENT - SEE FIGURE



4.0 (Continued...)

4.2 Pilot-Plant Studies

The laboratory calcination studies were valuable for learning basic characteristics of the salt decomposition but did not provide data sufficient for design of a production unit. It was assumed that the low yields and poor material balances in the small unit could be attributed to the small sized samples. The reaction seemed to be clean-cut and complete without complicating side reactions. However the quantity of residue available in the lab unit was so small it was quite impossible to determine its physical characteristics. Thus it seemed expedient to go to larger scale equipment to determine engineering design features which could not be anticipated from bench-scale experiments.

The original plan was to build pilot sized equipment in Chem-Seps' facilities. In the meantime it was found that pilot sized rotary calcination equipment was commercially available at the Bartlett-Snow-Pacific Company. There was a choice of running this equipment in Chem-Seps' or Bartlett-Snow-Pacific's facilities. Because of their know-how, the total costs involved, and the presence of adequate facilities, it seemed to be advisable to operated at Bartlett-Snow.

Based on the laboratory work there was no obvious reason why at least as good performance could not be expected on the larger scale equipment. In many ways there was more flexibility of control which would make the pilot scale equipment a better tool for checking variables. Because of the slow rate of warm-up in the lab equipment, it was difficult to determine an accurate relationship between hold-up time and rate of decomposition with increased temperature. With the larger continuous counter-current flow equipment it was anticipated that a more intensified and revealing study could be made.

Description of Pilot-Plant Calciner - The BSP pilot plant calciner is a vapor-tight rotary gas fired 6 1/2 I.D. stainless steeel unit. The heated zone is about 4 feet long. Retention time is controlled by varying inclination. Thermocouples indicated the temperature at the inlet and outlet points in the heated zone and in the center of the reaction zone. A screw solids feeder is normally used, but this was replaced with a small calibrated tank and throttling valve for introduction of concentrated nitrate salt solution. The off-gas scrubber and recovery system was crude, but considered adequate for material balance recoveries of nitric acid. All hot vapors were bubbled under water and a flowing stream of water was used to adequately remove the heat. During the runs it became evident that this was a very poor scrubber. A stainless steel bundle tube heat exchanger should have been purchased. (See Figures 4 and 5)

4.0 (Continued...)

Operation of Pilot Plant Calciner - In order to get a "feel" for the equipment operation, preliminary runs were made with aluminum nitrate and ferric nitrate salts. These salts were used because of the relative ease and low temperature at which they decompose. Thus, a basis of operation was established as to how to adjust the heat and liquid feed rate and maintain the proper temperature balance. There was no meter on the steam flow, but an excess was used. A crude measurement was made by taking the difference between the water input and outlet in the scrubber.

Discussion of Results - In summary, the decomposition of aluminum and iron nitrates proceeded without difficulty to yield oxide products of $Al_2O_3$ and $Fe_2O_3$. Recovery of nitric acid was 55% and 43% respectively. After examining this data it was suspected that the one stage water scrubber was less efficient than assumed since 100% yields had been obtained in laboratory equipment.

Recovery of nitric acid was very meager when the system was changed over to the nitrate salts of calcium, magnesium, sodium, and potassium. Recovery was only 1.3% to 3.6% of the nitrate input.

One of the most valuable checks on the degree of decomposition turned out to be only of qualitative value. An observation of the off-gas was made relative to the flow of steam. Brown fumes of $N_2O_4$ were noted when the steam was cut off; by increasing steam flow these were quenched. This seemed to confirm that nitric acid was a preferred product as long as sufficient water vapor is available.

Analysis of the calcined residue indicated greater degree of decomposition than did the recovery of acid, but also indicated an incomplete reaction. In general there seemed to be almost complete decomposition of the alkaline-earth nitrates but almost none of the alkali nitrates. Four separate batches were run at different temperature ranges. There was fairly good correlation of decomposition with temperature and a fairly good check of material balances and products. Note Tables IV and V and Figure 6. At the maximum temperature of 475° in the lowest temperature run, there was almost no decomposition of the alkali nitrates and about half of the alkaline earth nitrates. At maximum temperatures of 628° and 660°C, about 5% of the alkali nitrates formed hydroxides and up to 87% of the alkaline earths. When dropping down to 565°C the alkali hydroxide production dropped to 1.5%.

The calciner runs were made over about a two-day period and were cut short by a failure of the steam generator. This coupled with lack of on-site analytical facilities meant an end to the runs before the results could be observed and adjustments made for further runs.

After the results were analyzed it became evident that there was either an erroneous temperature indication in the pilot plant runs or more contact time was required. It is true that hold-up time in the lab unit was several hours whereas it was approximately 5 to 15 minutes depending on amount of blocking by cooled product in the pilot calciner. This fact is the only reasonable explanation for the incomplete reaction. Since the decomposition of calcium and magnesium nitrates

(continued....)

4.0 (continued...)

was preferred over sodium and potassium, it was reasonable to expect the decomposition of the former to be completed before the latter.

There was evidence in the lab tests that with temperatures above 600°C, one could expect some of the sodium and/or potassium to volatilize and appear in the condensate. In the pilot tests there were significant amounts of both alkali and alkaline earth ions in the condensate indicating that entrainment was the controlling factor rather than volatilization. The amount of entrainment was small, from 4 to 6%, but not a negligible factor.

At one point crystalline solids were deposited in the off-gas line before the water scrubber. These solids had the following composition: 94% $NaNO_3$, 0.6% $KNO_3$, 3.2% $Ca(NO_3)_2$, and 1.9% $Mg(NO_3)_2$. This confirms the laboratory findings that there is a problem of volatilization of NaOH and/or $NaNO_3$ under certain conditions. It is apparent that there is a critical temperature range in which to work in order to get decomposition without volatilization; it is possible to reflux $NaNO_3$ back into the reaction zone.

TABLE IV

THERMAL DECOMPOSITION OF ALKALI & ALKALINE EARTH NITRATES IN PRESENCE OF STEAM IN PILOT SCALE ROTARY CALCINER

Fee Material: 6 N Nitrate Solution -- On Equivalent Wt. Basis - 3.7% $KNO_3$
52.4% $NaNO_3$
25.4% $Ca(NO_3)_2$
18.6% $Mg(NO_3)_2$

Dry salt mixture by weight

| Run Code | Run Time Hrs. | Input Nitrate equivalents (0.98 eq/100g) Dry Salt | Temp °C | Condensate Equivalents | | | Calciner Residue Water Soluble Equivalents per 100 g | | | | Calciner Residue Filter cake eq. per 100g | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | H+ | Na | Ca-Mg | OH | Na | K | Ca-Mg | Nitrate | OH | Ca-Mg |
| #1-5 | 1.7 | 33.6 | 343-475° | 1.22 | 0.27 | 0.70 | 0.0010 | 0.60 | 0.043 | 0.236 | 0.98 | 0.27 | 0.306* |
| #6-#14 | 2.1 | 49.2 | 550°-628° | 1.05 | 1.18 | 1.09 | 0.0361 | 0.820* | 0.037 | 0.0926 | 0.90 | 0.32 | 0.354* |
| #15-#25 | 2.3 | 76.5 | 578-660° | 2.00 | 3.58 | 1.29 | 0.034 | 0.78* | 0.0415 | 0.039 | 0.884 | 0.50 | 0.46* |
| #26-#34 | 3.3 | 152 | 400-565° | 1.95 | 3.72 | 2.47 | 0.01 | 0.88* | 0.0467 | 0.169 | 1.00 | 0.48 | 0.36* |
| | | | | | | | 0.655 | 0.62* | 0.037 | 0.576 | 1.531 | 0.576 | 0.576* |

* Analysis indicates that proportion of sodium might be a little higher than original salt mixture indicates.

15-B

15-H

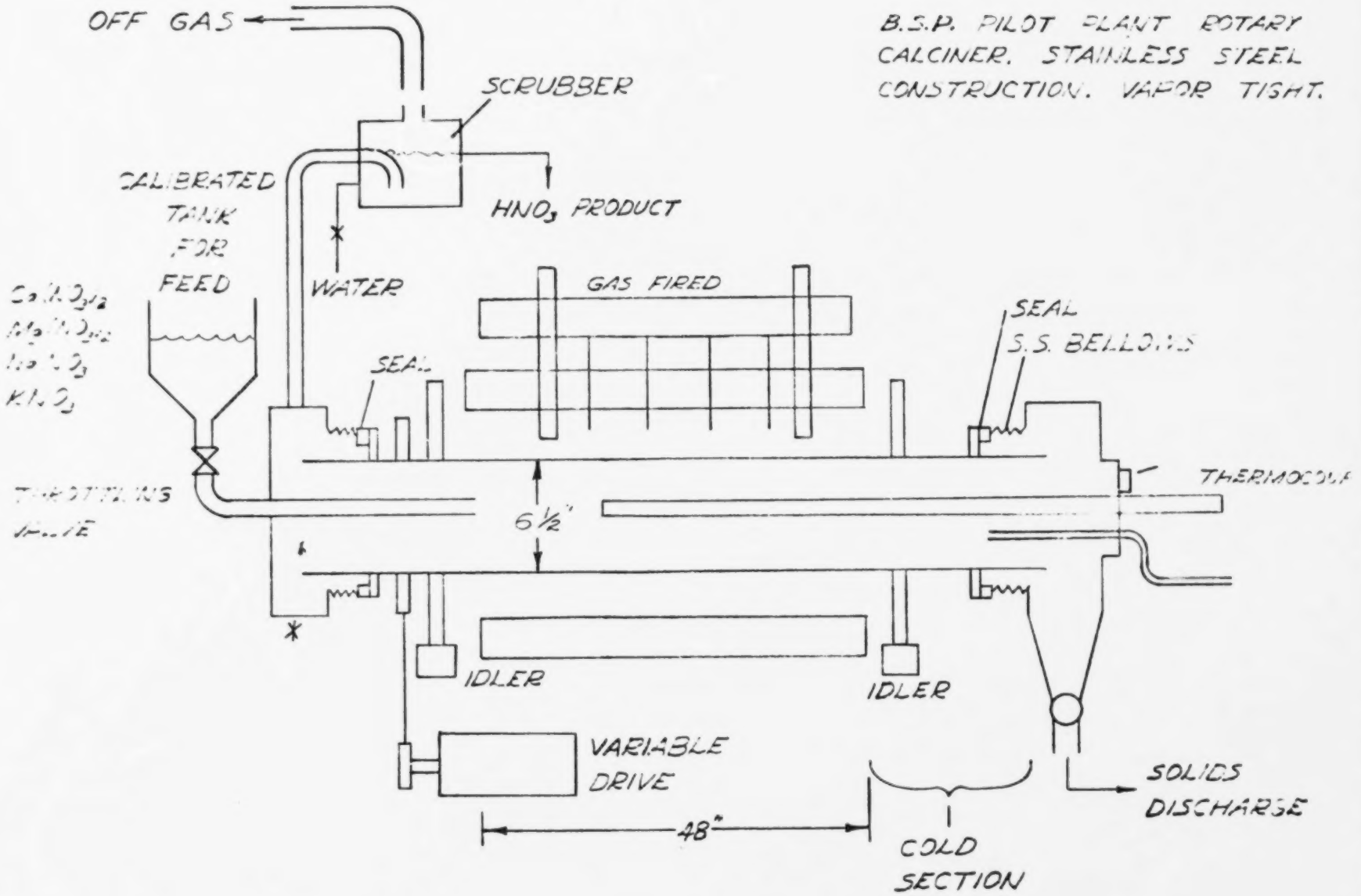
TABLE V

PILOT CALCINER RESIDUE YIELDS VS. TEMPERATURE

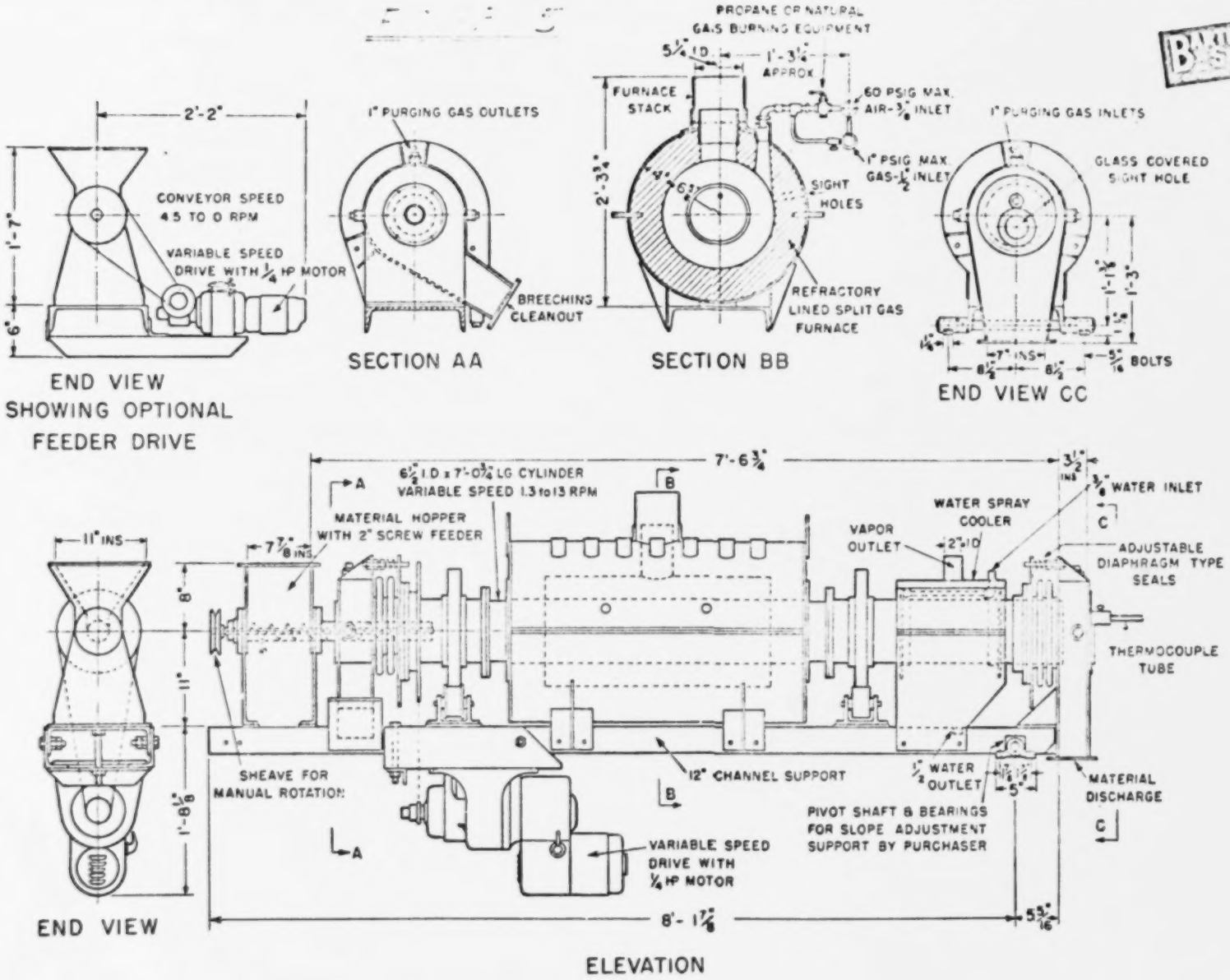
Feed - 3.7% $KNO_3$, 52.4% $NaNO_3$, .25.4% $Ca(NO_3)_2$ & 18.6% $Mg(NO_3)_2$

| Batch | Temp. Range | Hydroxide Yield | | Undecomposed Nitrate | Soluble Ca & Mg |
|---|---|---|---|---|---|
| | | Soluble | Insoluble | | |
| I | 343-475°C | nil | 47% | 64.3% | 41.0% |
| II | 550°-628°C | 5.5% | 56% | 59.0% | 16.1% |
| III | 400-565°C | 1.5% | 85% | 65.5% | 29.2% |

# FIGURE 4


OFF GAS
SCRUBBER
B.S.P. PILOT PLANT ROTARY CALCINER. STAINLESS STEEL CONSTRUCTION. VAPOR TIGHT.
CALIBRATED TANK FOR FEED
$HNO_3$ PRODUCT
WATER
GAS FIRED
SEAL
S.S. BELLOWS
SEAL
$Co(NO_3)_2$
$Mg(NO_3)_2$
$Ni(NO_3)_2$
$KNO_3$
THERMOCOUPLE
6½"
IDLER
IDLER
VARIABLE DRIVE
48"
SOLIDS DISCHARGE
COLD SECTION

C-51




# GAS-FIRED EXPERIMENTAL ROTARY CALCINER

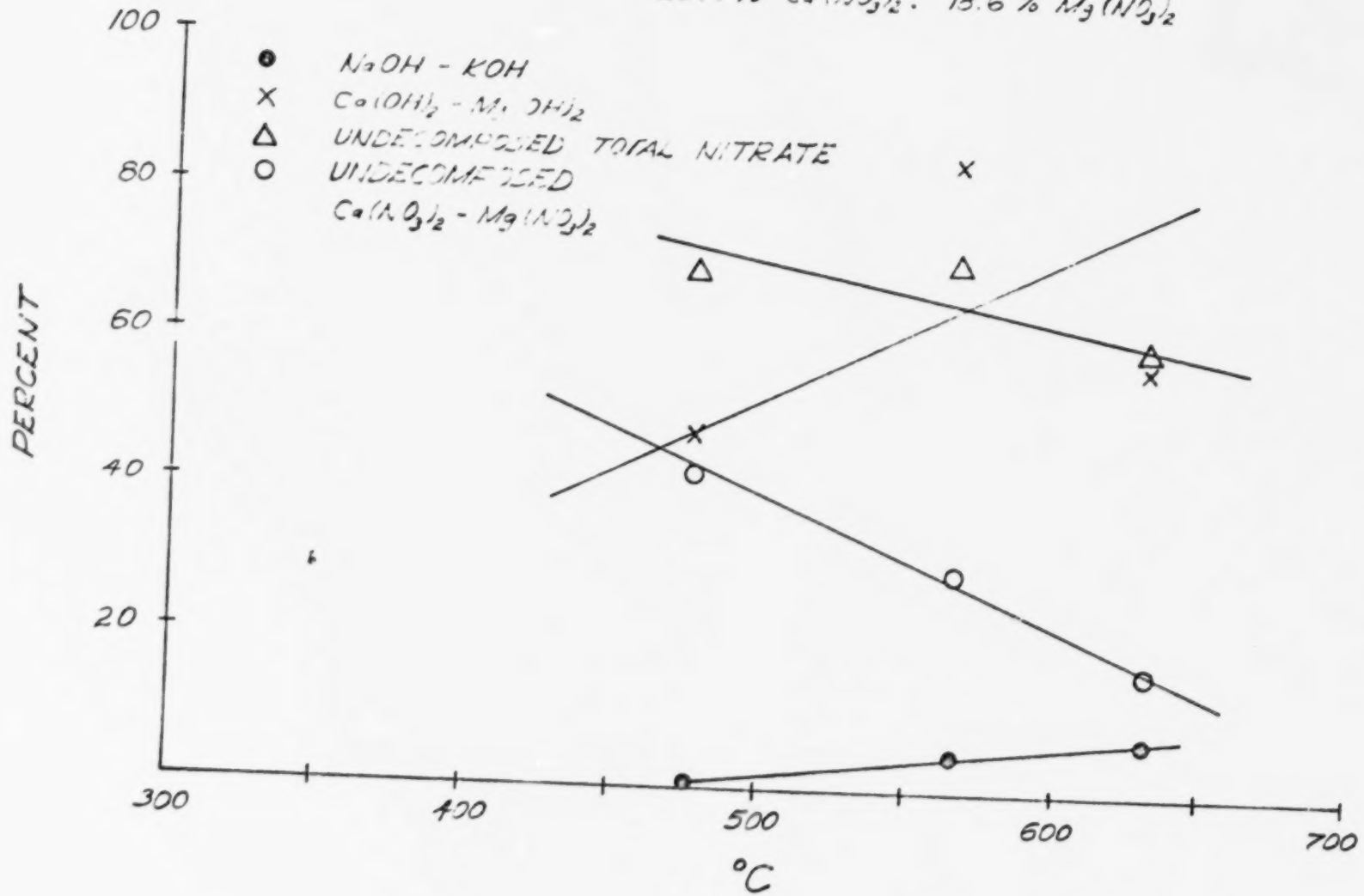
DRAWING No. GFC-117-3

FIGURE 8

PILOT PLANT CALCINATION

EQUIPMENT - SEE FIG. -

FEED - 3.7 % $KNO_3$. 52.4 % $NaNO_3$
25.4 % $Ca(NO_3)_2$. 18.6 % $Mg(NO_3)_2$




J-51

## 5.0 ION EXCHANGE STUDIES

### 5.1 Continuous Cation Exchange

A vital element of this flowsheet as an Advanced Waste Treatment Method is the contribution made to ion exchange by the Chem-Seps continuous counter-current ion exchange contactor. In summary, the main features are: (1) high throughput rate per unit equipment size, (2) concentrated regenerant wastes, and (3) savings in the consumption of regenerants.

Practically all the test work reported in this section has been carried on by Chem-Seps in related work and was not supported by this contract. However, it is one of the featured unit operations in the proposed flowsheet and probably the one most thoroughly demonstrated. Much of the work has been with softening instead of H-cycle exchange, but the comparative elution characteristics with concentrated brine and 4 M nitric acid are nearly identical.

The pioneering work on continuous softening was done on a one-two inch continuous ion exchange contactor using extra coarse resin, Dowex 50W, 8X, 16-20 mesh. Feed rates were 100 gpm/ft$^2$ for complete hardness removal from 300 ppm water and salt consumption 100% excess over stoichiometric[9]. Later larger scale runs were made on a four-inch - eight-inch contactor with standard mesh resin, Dowex 50W, X8, 20-50. Feed rates were 55 gpm/ft$^2$ and for the first time known a stoichiometric amount to 10% excess salt was used.[10] This same pilot unit was operated twenty-four hours per day, for a month at Oak Ridge National Laboratory to remove Sr-90 and Cs-137 from 100 ppm water on H-cycle using 4 M nitric acid. Hardness removal was complete. Strontium-90 removal was greater than 99.9%. cesium-137 greater than 90%, and the volume reduction factor from feed to regenerant waste was 500 to 1000.[11]

Chem-Seps next constructed an all stainless steel pilot unit with a sixteen-inch diameter loading section and a one-foot diameter regeneration section. See Figure 7. This was to be used to demonstrate softening, H-cycle cation exchange and hydroxide cycle anion exchange. The unit was on stream twenty-four hours per day at the Village of LaGrange, Illinois[2] from March until August, 1964 and at Worth, Illinois from August to October, 1964. Raw well water from 650 to 880 ppm hardness was reduced to 20 ppm with a stoichiometric to 10% excess of salt. This is considered a significant advance because in standard fixed-bed practice salt consumption is 100-200% excess (seldom lower than 80% excess even in very well operated plants).

Part of the work on a one-inch diameter laboratory contactor is reported here to indicate the regeneration efficiency with nitric acid and to relate it to other elution agents. Comparison is made with sodium chloride, nitric acid and hydrochloric acid, not to prove that one is better than the other, but to indicate that the work done with brine softening is indeed a demonstration of what may be expected of nitric acid. The arrangement of the test contactor used is indicated in Figure 8. Oak Ridge tap water, at 100 ppm hardness, was spiked with calcium chloride to increase the hardness to levels of 300 ppm to 5000 ppm as desired. During different tests salt and the common mineral acids were used as regenerants in concentration ranges of 3 to 5 N. (When using sulfuric acid, magnesium was substituted for calcium to avoid $CaSO_4$ formation in the resin bed.)

5.0 (continued...)

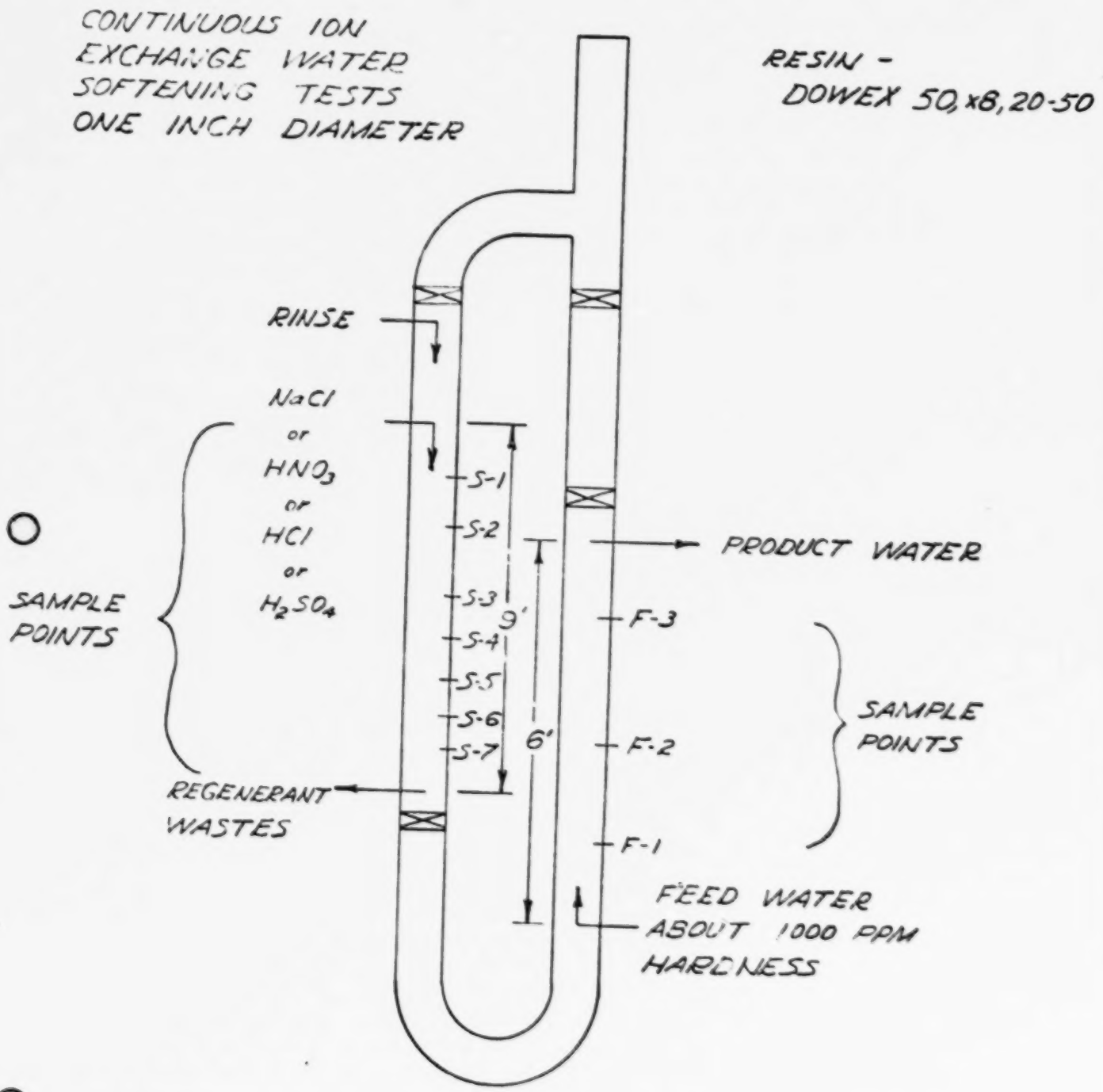
No outstanding or significant differences were noted in the efficiency of the various regenerants used. The strong acid styrene base cation exchange resins have a capacity of about 2.0 equivalents per liter. Characteristically in this type operation practically full capacity is utilized in loading, and to enable efficient regeneration, about half the cations are eluted. Figure 9 is a plot of the concentration profile of the hardness ion as a function of regeneration section length. The excess amount stripping agent and the degree to which loaded resin is stripped are shown. It is noted that with a minimal use of regenerant (NaCl near stoichiometric) the hardness ions are not swept off as fast, but nonetheless very adequately in that length (9 feet) to strip the resin to 0.7 eq/l. The 26% to 28% excess of H-ion for nitric and hydrochloric acids is greater than what is needed since the resin is stripped to less than 0.5 eq/l. It is also noted that solution strengths are maintained high and the concentrations of the cations are higher in the regenerant waste solution than sorbed on the resin.

Fig. 7

CUSTOMER: DEMONSTRATION UNIT (WATER)
LOCATION: Various
APPLICATION: Water Softening and demineralization
DIMENSIONS: 5' x 5' x 15' Overall
15" diameter loading section
12" regeneration section
MATERIALS: Stainless steel
Valves 3" diameter Crane Butterfly
CAPACITY: Soften to zero hardness 80 gpm raw water up to 1000 ppm hardness (60 grain)

CHEMICAL SEPARATIONS CORPORATION
*101 Midway Lane, Oak Ridge, Tennessee Area 615 482-1402*

# FIGURE 8

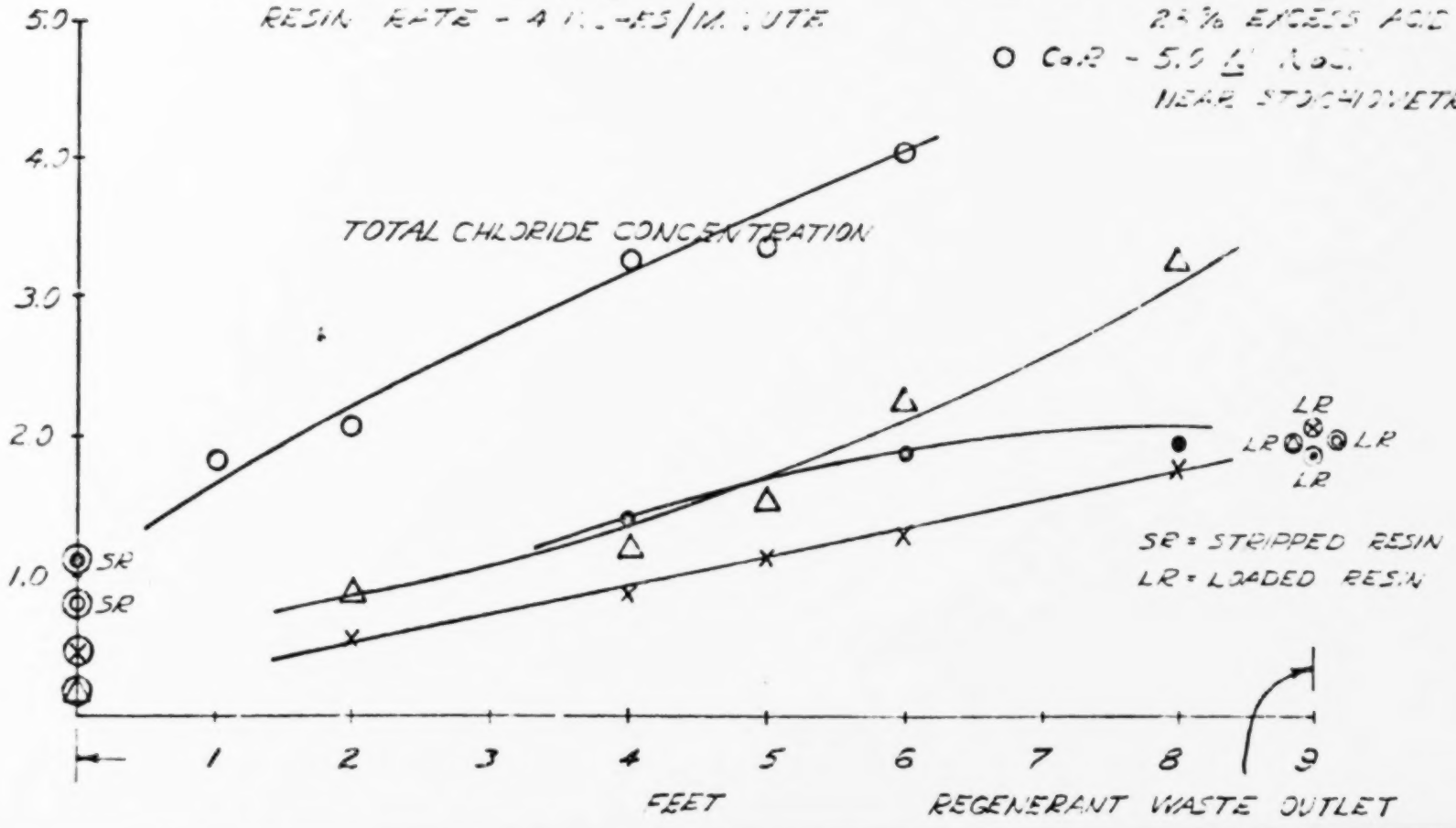

CONTINUOUS ION EXCHANGE WATER SOFTENING TESTS ONE INCH DIAMETER
RESIN - DOWEX 50, x8, 20-50
RINSE
NaCl
or
$HNO_3$
or
HCl
or
$H_2SO_4$
SAMPLE POINTS
S-1
S-2
S-3
S-4
S-5
S-6
S-7
9'
6'
PRODUCT WATER
F-3
F-2
F-1
SAMPLE POINTS
REGENERANT WASTES
FEED WATER
ABOUT 1000 PPM HARDNESS

# FIGURE 9

COMPARATIVE EFFICIENCY OF VARIOUS REQUIREMENTS USED FOR ION EXCHANGE TREATMENT OF WATER REGENERATION SECTION PROFILES - HARDNESS

EQUIPMENT:
ONE-INCH DIAMETER CONTINUOUS ION EXCHANGE UNIT
RESIN: DOWEX 50, X8, 20-50,
RESIN RATE - 4 INCHES/MINUTE

● MgC - 4.4 lb $H_2SO_4$ 10% EXCESS ACID
X CaC - 3.3 lb HCl 2.6% EXCESS ACID
△ CaC - 4.2 lb $HNO_3$ 2.5% EXCESS ACID
○ CaC - 5.0 lb NaCl NEAR STOICHIOMETRIC



5.0 (Continued...)

## 5.2 Continuous Anion Exchange Studies

The product of H-cycle cation exchange is a dilute-acid mixture of the salts present in the original feed. On hydroxide form anion exchange resin the driving force for acid sorption is great because it is an acid-base reaction to form water. Strong-base type resin will remove all anions; weak-base fails to sorb the weak acids such as silica or carbonate. Weak-base resin is considered because there is a limited amount of caustic available for regeneration. Regeneration may be accomplished stoichiometrically with weak alkali-- $NH_4OH$ -- which is not the case with strong-base resin. If there were adequate amounts of KOH and NaOH available to regenerate the strong-base resin, the weak-type would not be necessary. Since the weak-type may be regenerated with a weak base like $NH_4OH$, full utilization may be made of all the available alkali including the $Ca(OH)_2$ and $Mg(OH)_2$. This is accomplished by reacting the total calcination product, soluble and insoluble hydroxides, with ammonium salt regeneration waste to displace ammonia.

The weak-base type resin also has other inherent advantages of interest. Their nominal capacity is about 2.0 eq/l as compared to 1.2 for the strong-type. They are more stable chemically and temperature-wise and are not as easily poisoned. Exchange rates are slow as compared to the strong-type but fortunately this application involves characteristically fast acid-base neutralization type reactions.

Compared to the cation exchange experience described above in section 5.1, there has been very little work done with anion exchange. Previous experience has been with processing of uranium, tungsten, vanadium, molybdenium, caustic soda, certain waste streams, etc., but not water treatment. Test work was done on this project with a one-inch diameter laboratory contactor specifically to check out operating characteristics for water treatment. The primary objective was to determine degree of resin utilization, production rate per square foot, amount excess regenerant over stoichiometric, strength of regenerant waste, and if phosphoric acid would sorb as well as the other mineral acid. (See Figure 10)

Amberlite XE-168 weak-base resin was used first with hydrochloric acid and ammonium hydroxide. As soon as run conditions were established, mixed acids were substituted in the ratio they would occur under flowsheet conditions from H-cycle cation exchange. On an equivalent H-ion basis, the acids were 47.8% HCl, 35.6% $H_2SO_4$, 11.8% $H_3PO_4$, and 4.9% $HNO_3$. When the flow conditions were well balanced there was only a 2% excess of $NH_4OH$ over stoichiometric in the regenerant waste. Acid could not be detected in the product water stream. Resin flow rate was 3 inches per minute. Material balance on the basis of loading indicated 1.9 eq/liter capacity utilization and 2.18 eq/liter on the basis of regenerant consumption. Exchange zones for both cycles were very sharp and 3 ft. of section length was adequate in both operations. Of the acids listed, phosphoric acid is the least ionized, or the weakest acid. Its breakthrough was observed relative to chloride to determine if there was a preferential sorption. When overloading phosphate did break through first. As long as the resin wasn't loaded in excess there was no $H_3PO_4$ breakthrough.

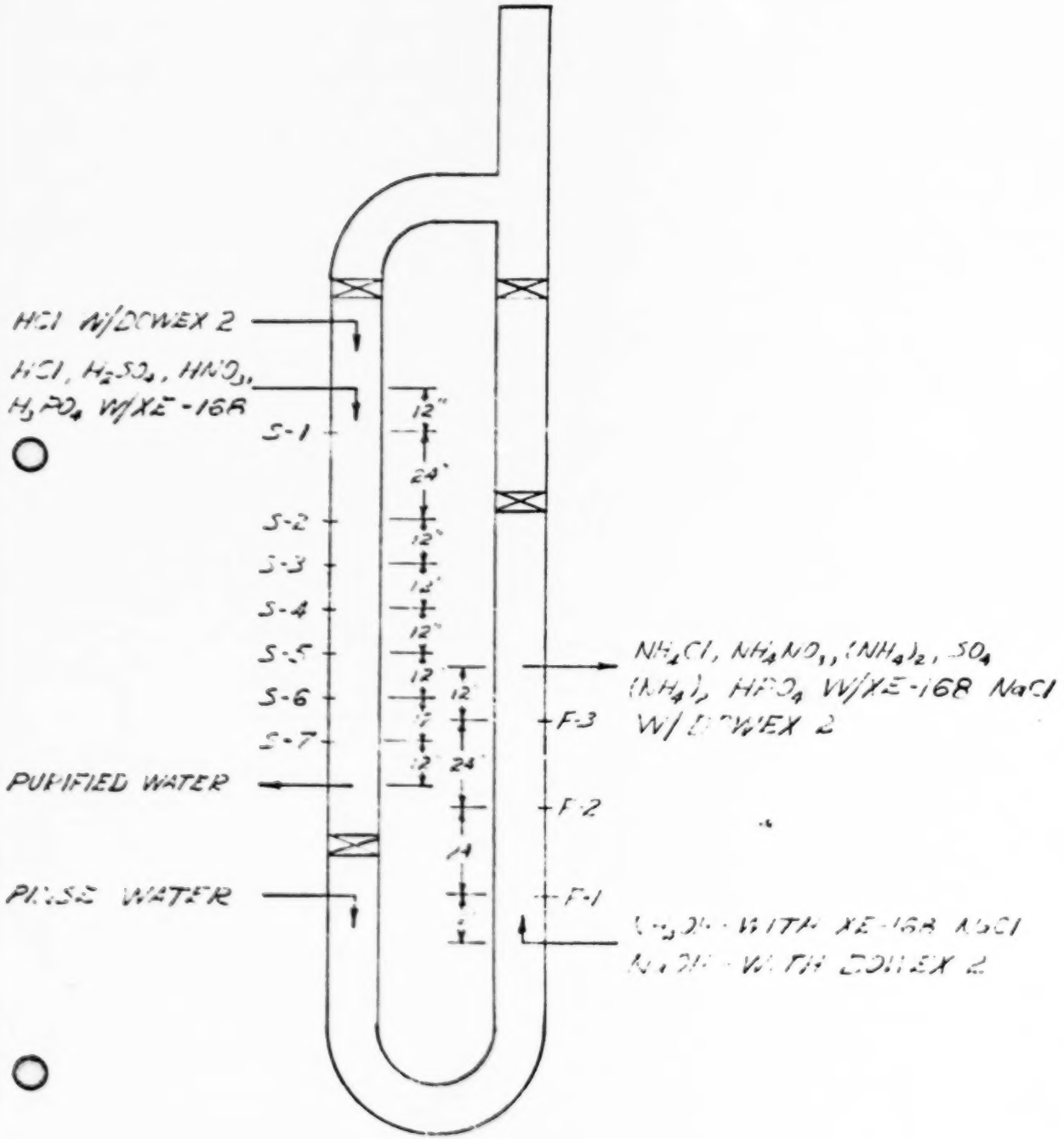
5.0 (Continued...)

Bicarbonate was not studied because it was not expected to sorb at all, but an interesting observation was made. At the interface between the incoming acid and hydroxide form resin there was formation of a gas pocket thought to be carbon dioxide. In acid, of course, $CO_2$ would be released. As the gas was pushed down into the alkaline resin it would re-adsorb and disappear. This tended to accumulate a larger and larger gas pocket of gas until finally steady state removal was attained. The fact that carbon dioxide is a gas means that it could not be removed by this resin , but certain other weak acids may be. (See Figure 11)

A continuous run was also made on strong-base resin. In the proposed flow-sheet a fixed bed is used because of the relatively slow loading rate with the "left-over" weak acids. If a decision were made to use strong-acid resin to do the complete job it would be necessary to know the minimum excess of sodium and potassium hydroxide which would be required to complete the regeneration. A short run was made using type II resin, Dowex 2, X8, 20-50 mesh. Only HCl was used as acid so it would be easy to follow analytically. On examination of the stripping profile, Figure 12, it is noted the strong base ROH-RCl exchange is not as "sharp" as the weak-base R-RHCl exchange and a greater section length is required. The excess hydroxide, measured in two ways analyzed 10% and 29%. This was probably more excess than necessary; very close to stoichiometric use of caustic may very well have been satisfactory.

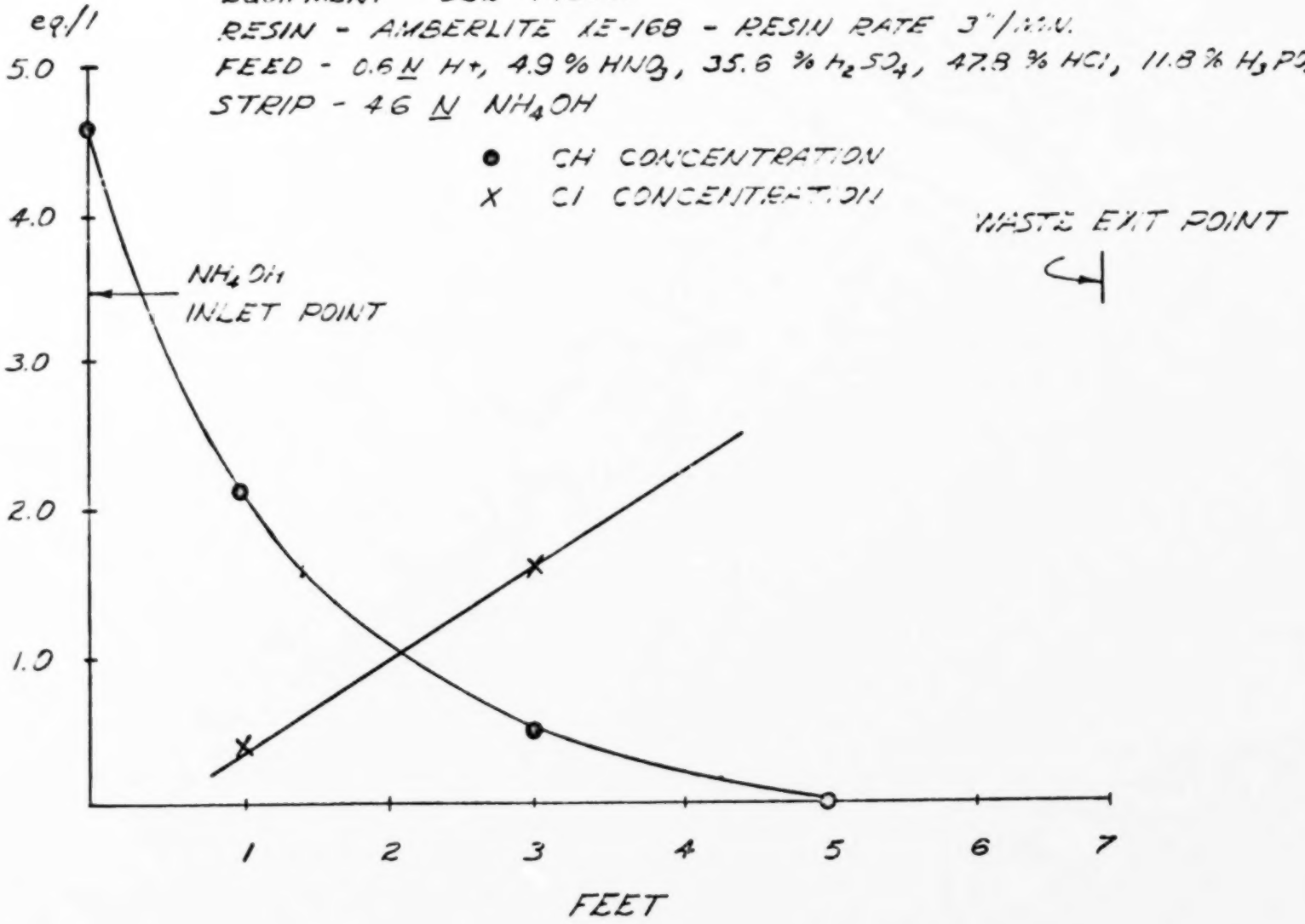
# FIGURE 10

LABORATORY CONTINUOUS ION EXCHANGE CONTACTOR
FOR WATER TREATMENT TESTS ONE-INCH DIAMETER



# FIGURE 11

WEAK-BASE RESIN REGENERATION WITH AMMONIA HYDROXIDE
REGENERATION SECTION CONCENTRATION PROFILE
EQUIPMENT - SEE FIGURE
RESIN - AMBERLITE XE-168 - RESIN RATE 3"/MIN.
FEED - 0.6 N $H^+$, 4.9 % $HNO_3$, 35.6 % $H_2SO_4$, 47.8 % HCl, 11.8 % $H_3PO_4$
STRIP - 4.6 N $NH_4OH$



# FIGURE 12

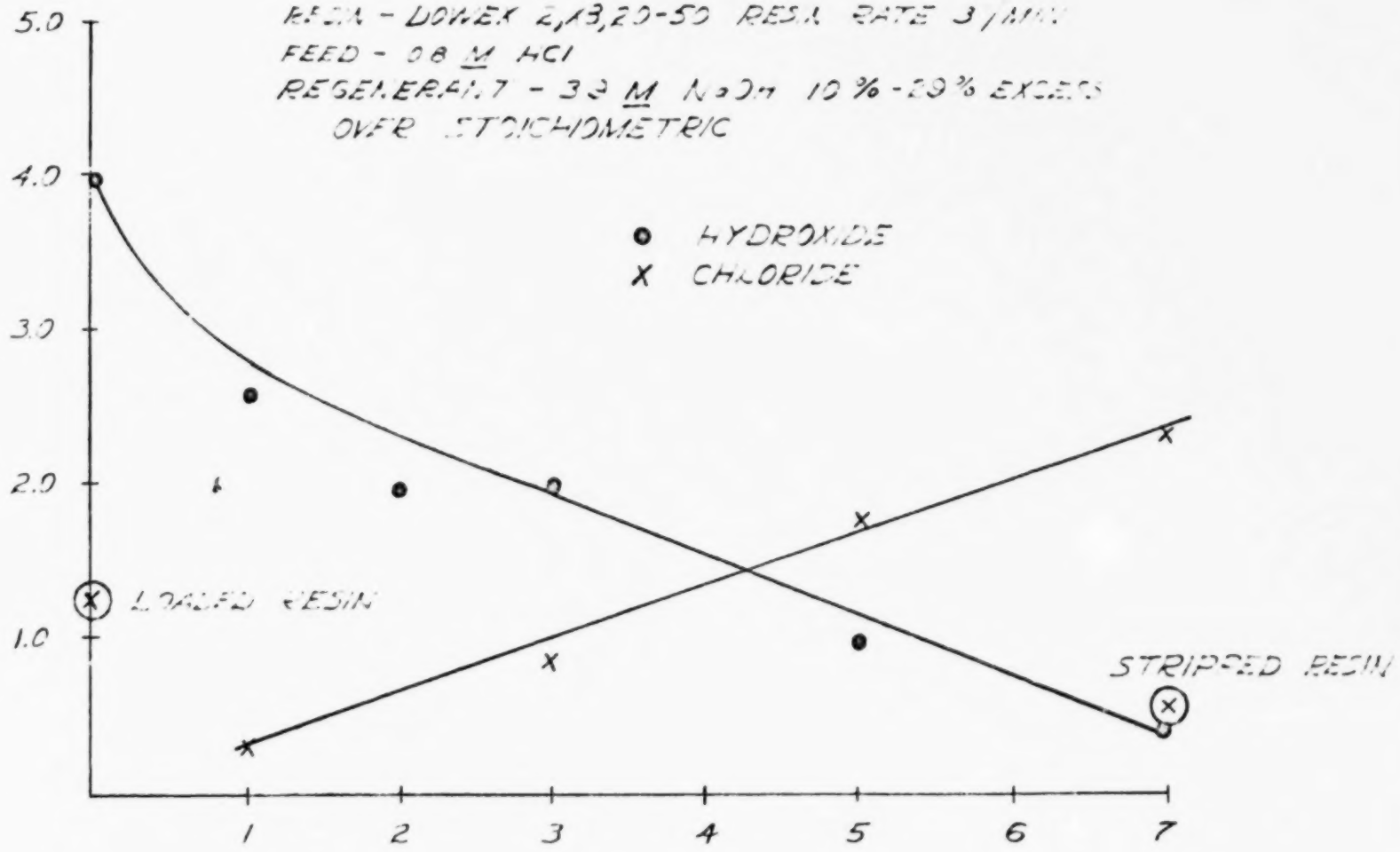
STRONG-BASE RESIN REGENERATION WITH SODIUM HYDROXIDE
REGENERATION SECTION CONCENTRATION PROFILE

EQUIPMENT - SEE FIGURE

RESIN - DOWEX 2, 1X8, 20-50 RESIN RATE 3 L/MIN

FEED - 0.8 M HCl

REGENERANT - 3.2 M NaOH 10% - 20% EXCESS OVER STOICHIOMETRIC



## 6.0 AMMONIA RECOVERY STUDIES

The weak-base regenerant, ammonia is too expensive to use once on a throw-away basis and it is necessary to establish a method of recycle. Ammonia can be regenerated for reuse, even by the insoluble hydroxides, $Ca(OH)_2$ and $Mg(OH)_2$, which otherwise might not be useful for anion resin regeneration. It is already a standard ion exchange practice to make use of lime (CaO or $Ca(OH)_2$) to release ammonia from ammonium salts. The Solvay process is a well-known, large-scale commercially used method for releasing ammonia from ammonium chloride by addition of lime.

For this proposed flowsheet it is planned to use the calciner residue, NaOH, KOH, $Ca(OH)_2$, and $Mg(OH)_2$. Lime has been used directly as an ion exchange reactant to make caustic soda from sodium chloride. Lime run directly in the ion exchanger in this manner is prohibited for water treatment because of the formation of insoluble $CaSO_4$, and/or $CaCO_3$ within the resin beads.

Because ammonia recovery is standard technology a large amount of effort was not expended. A few simple experiments were performed to confirm that there was no unforeseen problem. A mixture of ammonium salts was used equivalent to what would be expected from regeneration of weak-base anion exchange resin.

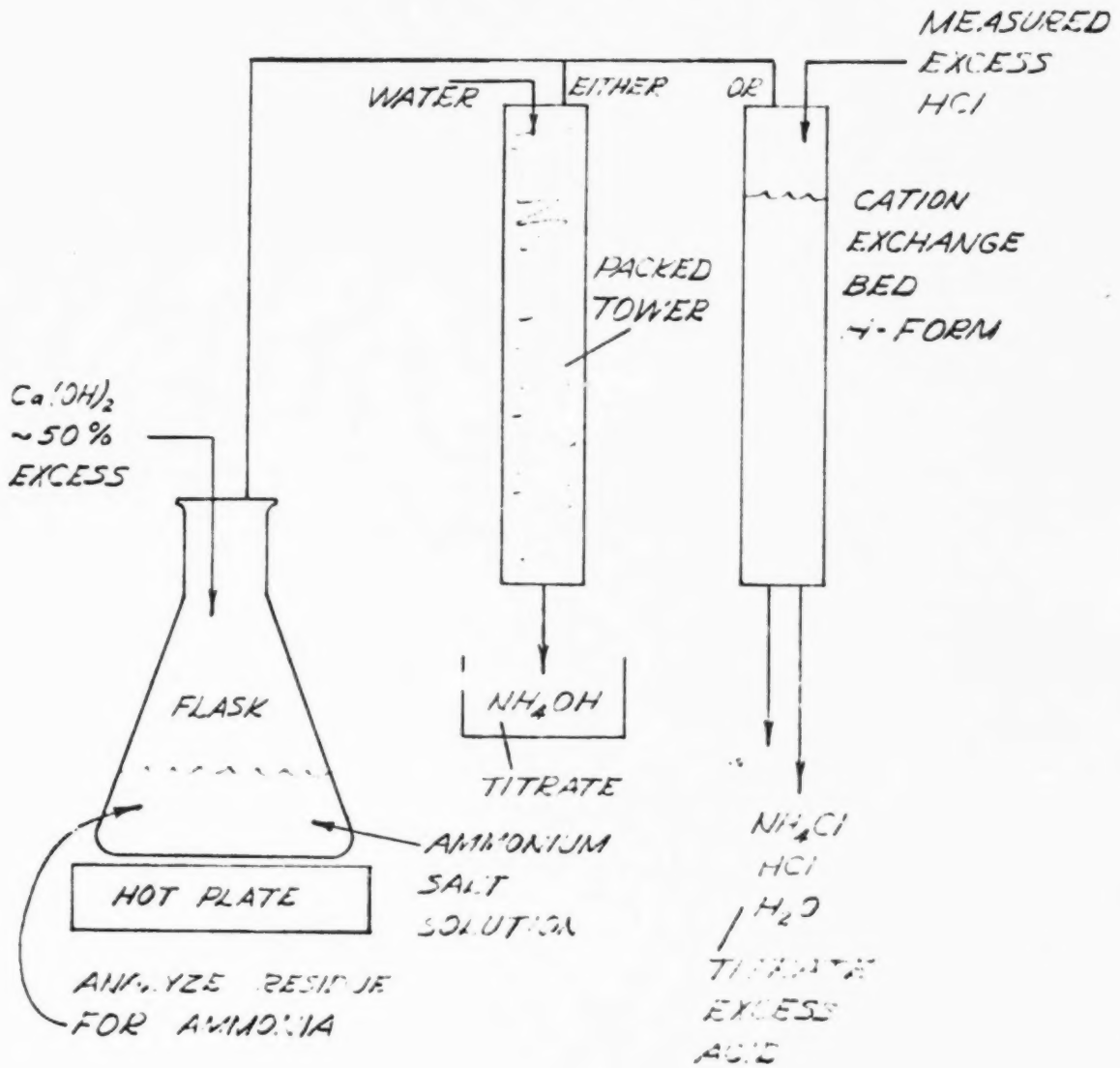
| | |
|---|---|
| $NH_4Ci$ | 50% |
| $(NH_4)SO_4$ | 34.0% |
| $(NH_4)_2\ HPO_4$ | 11.5% |
| $NH_4NO_3$ | 4.5% |
| | 100 % |

Lime as $Ca(OH)_2$ was added equivalent to 50% excess over stoichiometric. In the first experiments the ammonia was sorbed in a crude packed column and yields were only about 50%. For complete sorption the ammonia gas was run through a thoroughly regenerated ion exchange bed in the H-form. The ammonium ion was then eluted with a measured volume of standardized acid in excess and back titrated. The residue ammonium ion in the pot was analyzed using Nesslers reagent. On two test runs using the ion exchange sorption of ammonia, a 117% and 115% recovery was indicated. The corresponding residue of ammonia was 0.38% and 0.30%.

It was concluded from these short runs that close to 100 % of the ammonia is readily recoverable. (See Figure 13)

# FIGURE 13

## AMMONIA RECOVERY EXPERIMENT



## 7.0 COST ESTIMATE FOR A TEN MILLION GALLON PER DAY WATER PLANT

### 7.1 Capital Cost

The flowsheet indicated in Figure I is sized for $5 \times 10^6$ gpd because this is considered an optimum size for a single continuous ion exchange contactor. Projections for ten million and one hundred million gallon per day plants would require multiple units. A capital cost estimate for a ten million gallon per day plant is shown in Table VI.

In considering cost, each component has been estimated on the basis of a more-or-less complete package skid-mounted, with its own instrumentation, pumps, internal piping, etc. On this basis installation costs consist of bolting units to mounting pads and running interconnecting piping and electrical service. This is the explanation for seemingly lower-than-usual costs for piping, electrical, erection, etc.

Prices are readily available on large volume, standard items. Special large-scale equipment prices are difficult to arrive at. For instance, there is hardly a standard design for a decarbonator. Since test work is unfinished on the calcination equipment the cost is speculative. This estimate is not intended to be precise and is offered as a budget figure.

Building, land costs and interest are typical of municipal situations.

TABLE VI

## A. CAPITAL COST ESTIMATE FOR A 10 MGD WATER TREATMENT PLANT

| | | |
|---|---|---|
| 1. | Two (2) Continuous cation exchange contactors<br>8 ft. dia. loading section<br>3 ft. dia. stripping section with resin<br>500 $ft^3$ resin each, pre-erected, automatic control | $ 400,000 |
| 2. | Two (2) Continuous weak-base anion contactors<br>8 ft. diameter loading section<br>2 ft. diameter stripping section with resin<br>400 $ft^3$ resin each, pre-erected, automatic control | $ 400,000 |
| 3. | Four (4) Fixed-bed anion exchange polishers<br>10 ft. dia. - two on stream, automatic cycle, with resin (320 $ft^3$ resin each) | $ 120,000 |
| 4. | One (1) Redwood frame type decarbonator with blower | $ 40,000 |
| 5. | One (1) Bundle tube type stainless steel evaporator for 400,000 gpd 1600 $ft^2$ heating surface plus rectification tower | $ 150,000 |
| 6. | Two (2) Ammonia evolution reactor tanks at 100 gal. each | $ 15,000 |
| 7. | One (1) Calciner (not yet designed)<br>Contingency on parts not listed | $ 50,000<br>$ 100,000<br>$1,275,000 |
| 8. | Electrical connection | $ 50,000 |
| 9. | Interconnecting Piping | $ 100,000 |
| 10. | Installation -- mostly skid-mounted | $ 100,000 |
| 11. | Building 20,000 sq. ft. @ $7.50 | $ 150,000<br>$1,675,000 |
| 12. | Construction Fee @ 10% | $ 168,000 |
| 13. | Start-up & shake-down | $ 100,000 |
| 14. | Land | $ 20,000 |
| | TOTAL ESTIMATED CAPITAL COST | $1,963,000 |



(continued.....)

TABLE VI
( Continued.....)

B. AMORTIZATION & INTEREST

| | | |
|---|---|---|
| 1. Ion exchangers, piping, electrical & related costs<br>15 yr. amortization - | $87,600/yr | |
| 2. Decarbonator, evaporator ammonia reactor, calciner & related costs<br>10-yr. amortization | $46,400/yr. | |
| 3. Building<br>25-yr. depreciation | $ 6,600/yr | |
| TOTAL | $140,600/yr = | 3.85¢/1000 gallons |
| 4. Average interest over amortization period interest @ 4% - $77,000 ÷ 2 = $38,500/yr | | 1.08¢/1000 gallons |
| TOTAL | | 4.93¢/1000 gallons |

7.0 (Continued...)

7.2 Operating Cost

Operating cost is expressed as ¢/1000 gallons which will not be influenced much by the plant size, except for labor. One man per shift would be required for the 10 MGD plant, but assuming the equipment is automatic in operation the same manpower would be capable of handling multiple systems or larger units. The best yields of nitric acid in the test work were around 80%. Ninety percent is projected for this flowsheet and considered reasonable. The TVA nitric acid plant at Muscle Shoals operates at a 98% recovery of nitrogen gases when maximum oxidation and sorption are required; therefore 90% is not considered unreasonable. No credit is taken for excess of chemicals produced i.e. $CO_2$ and $NH_3$. Initial quantities of NaOH and $HNO_3$ for starting the plant are considered negligible.

Calculations for pumping cost and heat cost appear in the Appendix, Section 10. Three percent maintenance cost is usually about standard for this type equipment. Resin life is based on experience.

Ultimate disposal costs vary a good deal with method and location. The cost shown is for injection and was taken from a study by Louis Koenig-Research for Advanced Waste Treatment and appears in publication AWTR-8.

TABLE VII
OPERATING COST FOR A 10 MGPD PLANT

| | ¢/100 gallons |
|---|---|
| 1. Pumping<br>50 psi (4 contactor ) 50% efficiency and 1¢/kwh | 0.73 |
| 2. Heat Requirement<br>for evaporation and calcination<br>$6.2 \times 10^8$ BTU/day<br>Natural gas 1040 BTU/$ft^3$<br>50¢/1000 $ft^3$<br>Assume 50% heat recovery | 1.49 |
| 3. Nitric Acid<br>Assume $HNO_3$ recovery @ 90%<br>$HNO_3$ @ $30/ton at source<br>$HNO_3$ @ $45/ton delivered | 1.05 |
| 4. Operating Labor<br>One man per shift<br>@ $2/hr. , one supervisor per day, @ $3/hr | 0.72 |
| 5. Maintenance @ 3% of capital cost/Yr. | 1.60 |
| 6. Resin - 5 Yr. Life<br>Cation resin @ $25/$ft^3$<br>Anion resin @ $50/$ft^3$ | 0.78 |
| Total Cost Per 1000 Gallons | 6.37/1000 gallons |
| Ultimate Disposal by Injection<br>7000 ft., 9000 psi | .5¢/1000 gallon |
| TOTAL | 6.87¢/ 1000 gallons |

## 8.0 PROPOSED FOLLOWUP PROGRAM

### 8.1 Phase I

Pilot plant demonstration with prototype equipment to perfect equipment design and flowsheet conditions.

At the termination of this contract the performance of all unit operations in the flowsheet, except calcination, is considered well known and sufficiently proved. Enough information was obtained from the calcination studies to believe this operation is technically and economically sound.

It is recommended as a followup program that two types of calcination equipment be pilot planted, and then the most successful system be joined with the other components in an integrated pilot plant of the entire flowsheet. This pilot plant demonstration therefore would be accomplished in three steps:

1. Continuous rotary calciner operation with complete system off-gas condenser and scrubbers (See Figure 14).

   The pilot runs made on the rotary calciner were short and incomplete, but this type unit is considered to be an adequate and versatile tool capable of attaining all desired conditions except high production rate capacity per unit size. It is proposed that a Bartlett-Snow standard 6 1/4" stainless steel rotary calciner be purchased This unit should be adapted to maintain heat all the way to the end of the calcining tube on the solids exit end. Saturated solutions of individual or mixed nitrate salts would be fed with a diaphragm check valve pump. Provision would be made to meter steam and/or air, oxygen, or ozone. Iron oxide catalyst would be experimented with (Hanford Laboratory indicated beneficial effects). Enhancing effect of sugar (or similar, less expensive substitute) would be tried for breaking down nitrate at lower temperatures. Adequate condensers, scrubbers, and reoxidizers would be attached to handle all off-gas products. In connection with the latter, a visit would be made to the TVA Fertilizer Plant at Muscle Shoals and discussions held with their personnel who are reported expert in nitrogen gas handling (routinely oxidize ammonia to nitric acid with 98% yield).

2. Choice and testing of a compact high rate heat transfer system such as a sodium-potassium system (NaK). (See Figure 15).

   Much of the hardware used in Step I would be common to the high heat transfer system. This step is considered important because of the relatively low heat transfer capacity of a rotary calciner and the need to develop high production rate equipment. The decomposition vessel can be a standard bundle tube heat exchanger supplied by forced circulation of some molten heat exchange fluid, a molten salt or NaK. The heat exchange fluid may be heated by gas, oil, or electricity (calrod or resistance heat). Calrod electrical heat may be superior to a circulating fluid heat exchange media.

8.0 (continued...)

3. Construction and operation of a complete prototype plant to process in the range of 25,000 gpd of secondary effluent.

Step 3 will follow after successful operation of the calciner which would be sized to fit into a continuous ion exchange system using 4" to 6" diameter contactors. No highly critical items are involved that demand exacting capacity ratings and a well balanced completely integrated plant operation can be expected. The site can be selected later, but Oak Ridge has an adaptable secondary effluent waste stream.

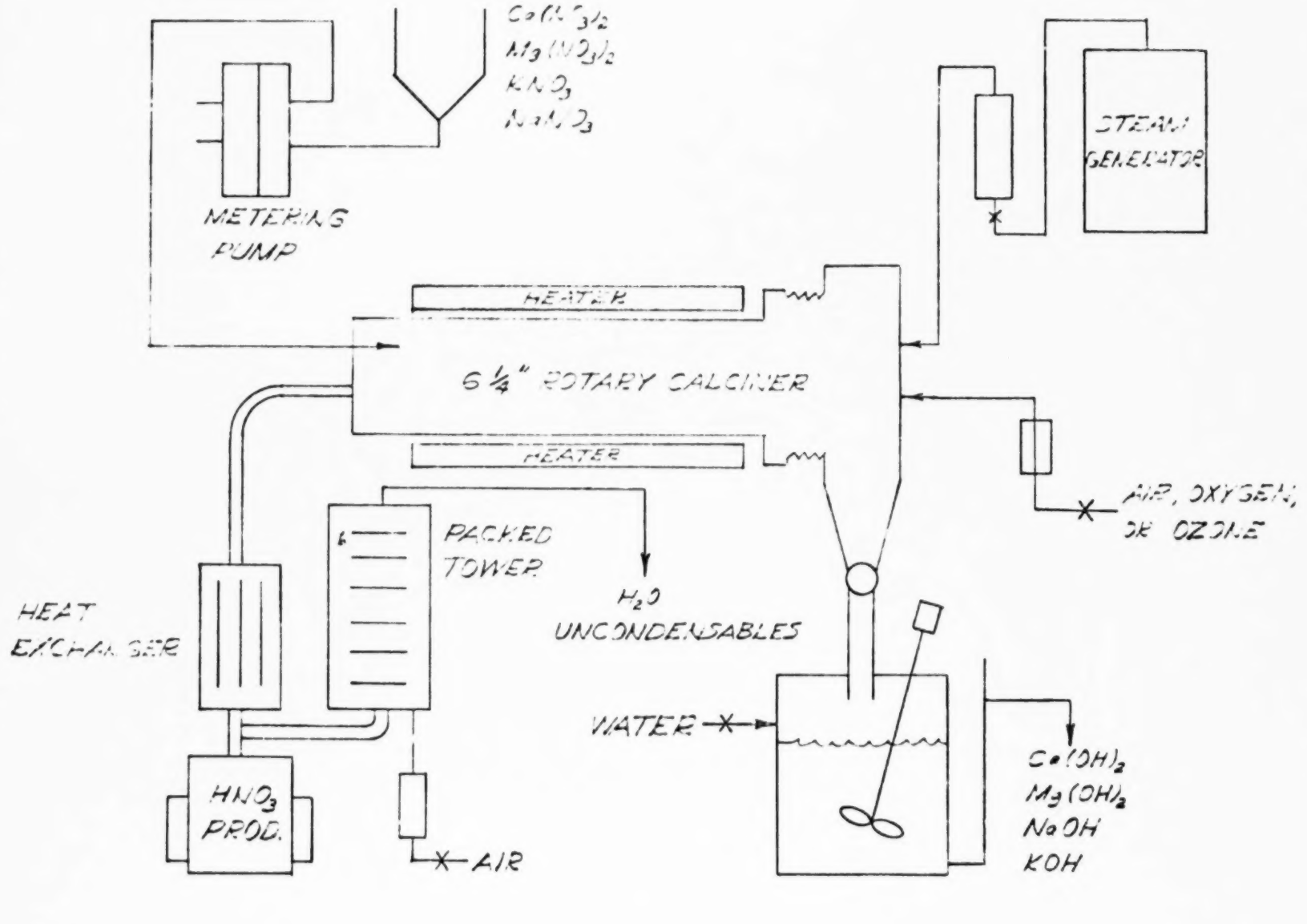
8.0 (Continued...)

Estimated Project Costs:

| | | |
|---|---|---|
| **Step. 1** | | |
| Steam Generator | $ 1,500 | |
| Diaphragm Feed Pump | 500 | |
| Condensers | 750 | |
| Scrub Towers | 750 | |
| Rotary Calciner - 6 1/4" diameter | $ 7,500 | |
| Tanks, Rotameters, Valves, Etc. | 2,000 | |
| Piping - Electrical | 2,000 | |
| Assembly | 1,500 | |
| Total Parts | $16, 500 | |
| Six Man-Months @ $2500 | $15, 000 | |
| Total | $31,500 | |
| **Step 2** | | |
| Additional equipment for high-capacity heat exchange | | |
| Electrical-Variacs and Calrod Heaters | $ 2,500 | |
| Canned Rotor Stainless Steel Pump | 500 | |
| Other Parts & Materials | 2,000 | |
| Piping, Electrical, Assembly | 2,500 | |
| | $ 7,500 | |
| Four Man-Months of Testing @ $2500 | 10,000 | |
| Total | $ 17,500 | |
| **Step 3** | | |
| Calcination System from Step I or 2 | | |
| Two (2) 4-6" dia. Contactors @ $30,000 | $60,000 | |
| One (I) Decarbonator | 2,000 | |
| One (I) Ammonia Scrubbing Tower | 2,000 | |
| Other Items-Tanks, Pumps, Compressors, Etc. | 10,000 | |
| Supplies, Reagents, Etc. | 15,000 | |
| Interconnecting Piping, Electrical, Installation | 10,000 | |
| Demonstration Facilities-Site, Bldg, Etc. | 30,000 | |
| | $129,000 | |
| One Man-Year Operation @ $2500/Month | 30,000 | |
| Total | $159,000 | |
| TOTAL ESTIMATED PHASE I COST | | $208,000 |

# FIGURE 1

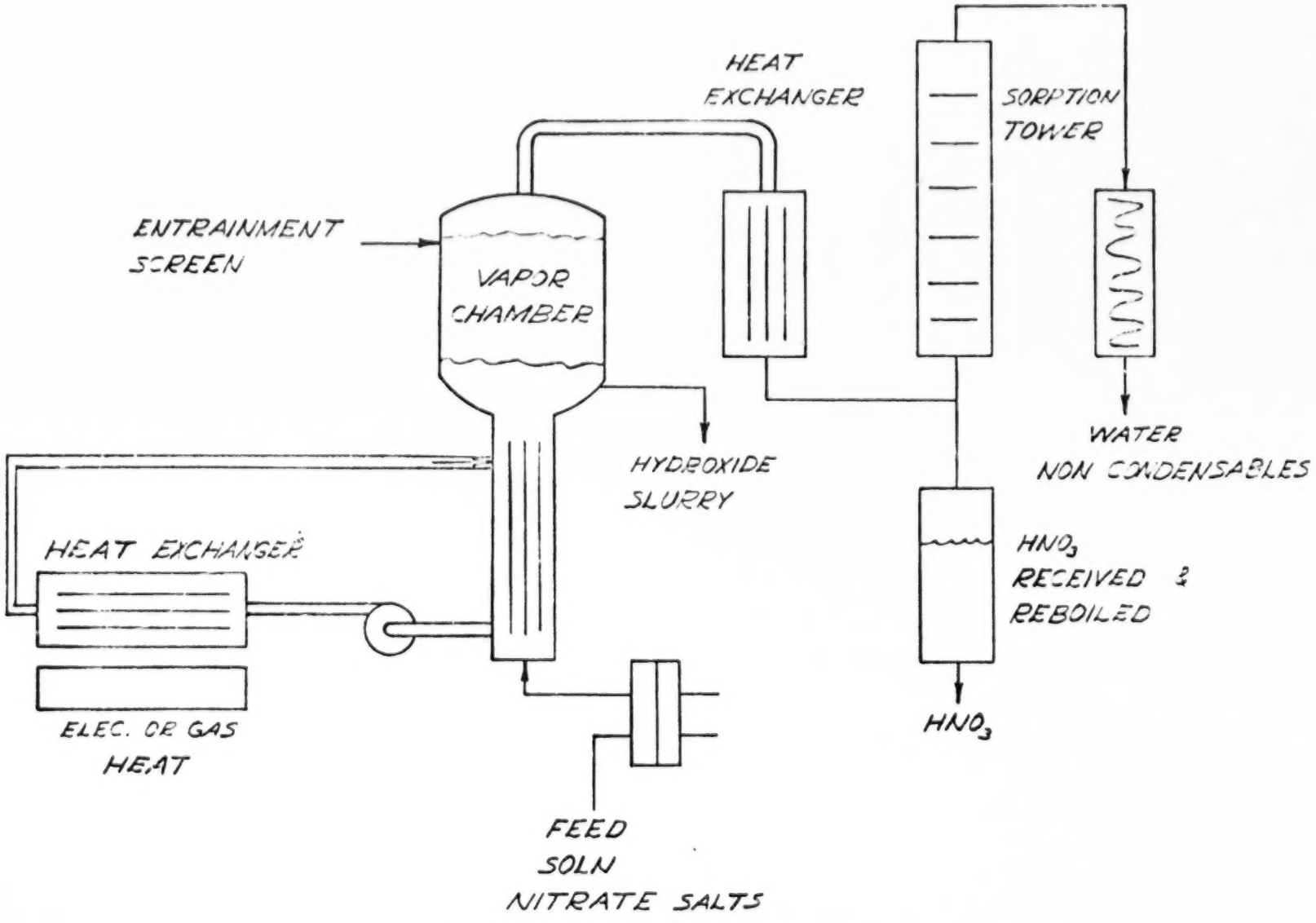
## ROTARY CALCINER - OFF GAS SYSTEM PILOT PLANT




24.B

# FIGURE 15

## HIGH HEAT TRANSFER SYSTEM




24-2

8.0 (Continued...)

8.2 Phase II

Commercial-scale demonstration (several million gallons per day) to demonstrate the economics.

With detailed flowsheet conditions and equipment design being determined in Phase I, the final step in the development of this system would be a full-scale demonstration, similar to what the Interior Department through the Office of Saline Water has done with the various desalination methods. It is proposed that a small community be selected which has a water problem, and this system be installed to demineralize their complete water supply.

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## 10.0 APPENDIX

### 10.1 Secondary Effluent Analysis & Flowsheet Calculations

The difficulty of choosing a typical water was resolved by using selected information supplied by the USPHS. The following is a tabulation of average secondary effluents in Eastern and Western USA. For flowsheet purposes the highest values are used which are indicated by a circle around the number.

AVERAGE SECONDARY EFFLUENT

| Component | Eastern | Western |
|---|---|---|
| BOD | 17 | 27 |
| COD | 97 | 218 |
| ABS | 5 | 7 |
| Na | 73 | (150) |
| K | 11 | (17) |
| $NH_4$ | (24) | 18 |
| Ca | 60 | (62) |
| Mg | 20 | (27) |
| Cl | 83 | (145) |
| $NO_3$-$NO_2$ | 12 | (16) |
| $HCO_3$ | 258 | (327) |
| $SO_4$ | 83 | (108) |
| $SiO_3$ | 22 | (53) |
| $PO_4$ | 20 | (36) |
| Hardness | 228 | 288 |
| TDS | 497 | 826 |
| pH | 7.3 | 7.4 |

Flowsheet Calculations for $5 \times 10^6$ GPD

5,000,000 gal. = 18,930,000 liters

| | | | | Per Day |
|---|---|---|---|---|
| K | $- 18.93 \times 10^6$ | $\times$ 0.017 gl = 322 Kg | = | 710 lbs |
| Na | | $\times$ 0.150 = 2840 | = | 6250 |
| Ca | | $\times$ 0.062 = 1175 | = | 2585 |
| Mg | | $\times$ 0.027 = 511 | = | 1128 |
| $HCO_3$ | | $\times$ 0.327 = 6200 | = | 13640 |
| $SO_4$ | | $\times$ 0.108 = 2045 | = | 4500 |
| Cl | | $\times$ 0.145 = 2740 | = | 5980 |
| $PO_4$ | | $\times$ 0.036 = 680 | = | 1495 |
| $NO_3$ | | $\times$ 0.016 = 303 | = | 666 |
| $SiO_3$ | | $\times$ 0.053 = 1000 | = | 2200 |
| $NH_4$ | | $\times$ 0.024 = 454 | = | 1000 |

10.0 (Continued...)

10.1 Flowsheet Calculation for $5 \times 10^6$ GPD (continued...)

| | | | PER DAY Kg | = | Lbs |
|---|---|---|---|---|---|
| $KNO_3$ | $\frac{101}{39} \times 322$ or 710 | = | 633 | = | 1640 |
| $NaNO_3$ | $\frac{85}{23} \times 2840$ or 6250 | = | 10,500 | = | 23200 |
| $Ca(NO_3)_2$ | $\frac{164}{40} \times 1175$ or 2585 | = | 4820 | = | 10600 |
| $Mg(NO_3)_2$ | $\frac{148}{24} \times 511$ or 1128 | = | 3160 | = | 6950 |
| $NH_4NO_3$ | $\frac{80}{18} \times 454$ or 1000 | = | 2020 | = | 4455 |
| $CO_2$ | $\frac{44}{61} \times 6200$ or 13640 | = | 4470 | = | 9850 |
| $H_2SO_4$ | $\frac{98}{96} \times 2045$ or 4500 | = | 2095 | = | 4600 |
| HCl | $\frac{36.5}{35.5} \times 2740$ or 5980 | = | 2820 | = | 6150 |
| $H_3PO_4$ | $\frac{98}{95} \times 680$ or 1495 | = | 700 | = | 1540 |
| $HNO_3$ | $\frac{63}{62} \times 303$ or 666 | = | 308 | = | 676 |
| $HN_3$ | $\frac{17}{18} \times 454$ or 1000 | = | 430 | = | 945 |

| Cation Exchange Load | | Eq/Min | Eq/ Day |
|---|---|---|---|
| K | 322,000g/39 | -- | 8,250 |
| Na | 2,840,000 g/23 | -- | 123,500 |
| Ca | 1,175,000g/20 | -- | 58,700 |
| Mg | 511,000g/12 | -- | 42,700 |
| $NH_4$ | 454,000g/18 | -- | 25,300 |
| Total | | 180 | 258,450 |

10.0 (Continued...)

10.1 (Continued...)

Decarbonator Load

95% of $CO_2$ - 9360 lbs/day

| Weak - Base Anion Exchange Load | | Eq/min | Eq/day |
|---|---|---|---|
| $H_2SO_4$ | 2,095,000/49 | -- | 42,600 |
| $HCl$ | 2,820,000/36.5 | -- | 77,000 |
| $H_3PO_4$ | 700,000/49* | -- | 14,300 |
| $HNO_3$ | 308,000/63 | -- | 4,880 |
| Total | | 96 | 138,780 |

* $H_3PO_4$ sorbs as divalent ion on weak-base resin

| Strong-Base Anion Exchange Load | | Eq/min | Eq/day |
|---|---|---|---|
| $H_2CO_3$ | - (5% of original) 223,000/22 | -- | 10,300 |
| $SiO_3$ | - 1,000,000/36 | -- | 27,800 |
| | | 26.5 | 38,100 |

Available Hydroxides

| | Kg/day | Lb/day | Eq/day |
|---|---|---|---|
| KOH | 463 | 1,020 | 8,250 |
| NaOH | 4960 | 10,910 | 123,500 |
| | | | 131,750 |
| $Ca(OH)_2$ | 2170 | 4770 | 58,700 |
| $Mg(OH)_2$ | 1240 | 2730 | 42,700 |
| | | | 101,400 |

10.0 (Continued....)

10.2 Calciner Heat Calculations

Basis for Heat of Decomposition of Solutions at 600°C

Start with solution at 25°C

Heat solution to 600°C , then decompose. Assume no heat of solution or state changes. Include only three sources of heat:

1. Heat of reaction at 600°C
2. Specific heat to raise nitrate salt to 600°C
3. Heat to vaporize and superheat water to 600°C

Step (1) includes the difference in heats of formation at 25°C of (products) minus (reactants) = $\Delta H25^{\circ}$ the heat reaction at 25°C.

The heat of reaction at 600°C ( $\Delta H_{600^{\circ}}$) equals (specific heat of the reactants) time the change of temperature plus $\Delta H25^{\circ}$.

Step (2) --Only the nitrate salt is included in this step because all the water is heated to 600°C in step (3). The specific heat of nitrate compounds are not equal to each other for elevated temperature because they start to decompose before 600°C, but the resulting hydroxides have approximately the same specific heat.

Step (3) --The heat for superheated steam at atmospheric pressure was taken from Perry's Chemical Engineering Handbook , 4th Edition, equal to 1591 BTU/lb. at 600°C equal to 874 Kg Cal/Kg.

| Reaction | Kg | Heat of Reaction $\Delta H25$ KCal/M | $\Delta H^{\circ}600$ KCal/M | $\Delta H^{\circ}600$ KCal/Kg | heat raise chem. temp. KCal/Kg | total chem. heat to decomp @600°C KCal |
|---|---|---|---|---|---|---|
| $NO_3$---KOH | 833 | 47.5 | 40.9 | 406 | 163 | 470,000 |
| $a(NO)_2$--$Ca(OH)_2$ | 6930 | 53 | 50 | 303 | 140 | 3,080,000 |
| $ig(NO_3)_2$--$Mg(OH)_2$ | 3160 | 66 | 64 | 428 | 142 | 1,800,000 |
| $laNO_3$-- NaOH | 10,500 | 31 | 28 | 328 | 247 | 8,600,000 |
| | | | | | | 13,950,000 |
| | | | | | | $14 \times 10^{+8}$ |

| /ater | Steam | | | |
|---|---|---|---|---|
| 5°C | 600°C | ) | 849 Kg Cal/Kg | |
| | 1112°F | ) | 158,500 Kg | $1.34 \times 10^{+8}$ |

Grand Total (179,923 Kg) $1.48 \times 10^{+8}$ KgmCal

( 830 Kgm Cal/Kg
( 1490 BTU/#

10.0 (Continued...)

10.2 Calciner Heat Calculations (continued....)

| | Mol. Wt. | PHYSICAL DATA Kg Cal/Mol Heat of Formation @ 25°C $H^{\circ}_{25}$ | g Cal/gm°c specific heat CP | Cal. avg. spec. heat 0-600°C g Cal/Gm°C CP | Calc. avg. spec. heat 0-600°C KgCal/Mol°C |
|---|---|---|---|---|---|
| $KNO_3$ | 101 | -117.7-C | .214-0-S<br>.240-100-S | 0.292 | 0.029 |
| KOH | 56 | -101.7-C | .25 assume | 0.25 | 0.014 |
| $Ca(NO_3)_2$ | 164 | -224.0-C | .25 assumed | 0.25 | 0.041 |
| $Ca(OH)_2$ | 74 | -235.8-C | .26-O-S<br>.288-50-S | 0.38 | 0.028 |
| $Mg(NO_3)_2$ | 148 | -166.32-C | 25 assumed | 0.25 | 0.037 |
| $Mg(OH)_2$ | 58 | -165.8-C | .295-O-SA<br>.295-900-S | 0.29 | 0.017 |
| $Na(NO)_3$ | 85 | -101.-C | .247-O-S<br>.270-50-S | 0.42 | 0.036 |
| NaOH | 40 | -102.-C | .25 assumed | 0.25 | 0.010 |
| $H_2O$ | 18 | 68-L | 1.0 | 1.0 | 0.018 |
| $NO_2$ | 46 | 8-g | .23-400-g | .23 | 0.011 |
| $N_2O_5$ | 108 | 3-g | .23-400-g | .23 | 0.025 |

State of Compound Example Cp- Specific heat (.214 value of $KNO_3$ at 0°C and solid)

g - gas
c - crystal
s- solid %

Data not denoted for Long's Chemistry Handbook -10th Edition
A - North American Combustion Handbook, 1952

10.0 (Continued....)

10.2 Calciner Heat Calculations (continued ..)

$$2\,KNO_3 + H_2O \longrightarrow 2\,KOH + N_2O_5$$

$H_{(25)}$ $2\,(KNO_3)$ $-(-235.4)$ $-(-68.0)$ $303.4$

$2KOH = (-203.4)$

$N_2O_5 = (3.0)$ $-206.4$

$303.4$
$206.4$

$+97.0$

Heat of formation KCal/2 Mol of $KNO_3$ $\boxed{H_{25^\circ} = +47.5}$ KCal/Mol $KNO_3$ @ 25

$\Delta H^{600} = (\Sigma\,(Cap) - \Sigma\,Cp\,(R))\ \Delta T + \Delta H_{25} =$

| | | |
|---|---|---|
| .028 | 058 | |
| 025 | 018 | |
| (053 | - 076) | (575 |

$$H_{600^\circ} = \frac{(-.023)\ (575)}{2} \quad (47.5) =$$

$H_{600^\circ}$ - 6.6 47.5 = 40.9 KgCal/Mol $KNO_3$

Specific Heat

$Cp\ (25\text{-}600) = (.029)\ (575) = 16.5$ KgCal/Mol $KNO_3$

$Cp\ (KNO_3)\ T_{600\text{-}25}$

Heat of Decomposition at 40.9 KgCal/Mol $KNO_3$

600°C $\quad \frac{16.5}{57.4}$

$$Ca(NO_3)_2 + H_2O \longrightarrow Ca(OH)_2 + N_2O_5$$

$224 + 68 \longrightarrow 236 + 3$

| | | |
|---|---|---|
| 224 | 236 | 292 |
| 68 | 3 | 239 |
| 292 | 239 | 53 |

$H25^\circ$ + 53 KgnCal/Mol $Ca(NO_3)_2$

$$H_{600^\circ} = (.028) - (.041)\ (.025) \quad (.018)$$

$(.053\text{-}059)\ (575) + 53 = 50$ Kgm Cal/Mol $Ca(NO_3)_2$

Heat raise chemical to 600°C

(.041) (575) = 23 KgCal/Mol

10.0 (Continued...)

10.2 Calciner Heat Calculations (continued...)

$$Mg(NO_3)_2 + H_2O \longrightarrow Mg(OH)_2 + N_2O_5$$

| | | |
|---|---|---|
| 166 | 165 | 234 |
| 68 | 3 | 168 |
| 234 | 168 | 66 |

$\Delta H_{250} = +$ **66 Kgn Cal/Mol $Mg(NO_3)_2$**

$$\Delta H_{600} = \left[\begin{pmatrix}0.017\\.025\\.042\end{pmatrix} - \begin{pmatrix}.037\\018\\.045\end{pmatrix}\right] (575) + 66 = +64 \text{ Kgm Cal/Mol } Mg(NO_3)_2$$

Specific Heat

$$\left[0.037\right] \quad 575 = \boxed{21 \text{ Kg} \quad \text{Cal/Mol } Mg(NO_3)_2}$$

428
142
570

$$2 \quad Na(NO_3) + H_2O \longrightarrow 2\,(NaOH) + N_2O_5$$

$$202 + 68 \longrightarrow 204 + 3$$

270
207

$\Delta H_{250} = 63$ Kgn Cal/2 M $NaNO_3$ = $\overline{\Delta H25}$ = 31 Kgn Cal/Mol $NaNO_3$

$$\overline{\Delta H_{600}} = \left[\begin{pmatrix}.034\\.025\\.079\end{pmatrix} - \begin{pmatrix}.072\\.018\\.090\end{pmatrix}\right] \frac{575}{2} + \frac{63}{2} = \boxed{28 \text{ KgnCal/Mol } NaNO_3}$$

Specific Heat

(.036) (575) = **21 Kgn Cal/Mole**

247
328
575

10.0 (Continued)

10.3 Ammonia Scrub Tower Calculations

A scrubbing tower for ammonia recovery was considered a standard unit operation and for the flowsheet conditions indicate (Figure 1 ) was calculated as follows:

Packed Height = 6 ft.
Diameter 14"

Packing = 1" Berl Saddler (Ceramic)

Flow Rates: Water = $\frac{238 \text{ lb. ft}^2}{\text{Hr.}}$ Exit gas = 2.5 - 12.5 lb/hr

Strength of Outcoming $NH_3$ 68 gm/liter 4 M
= 6.8 Hrs/100 Hr. of Water

Operating pressure - 1 atm.
Operating Temperature - 70°F
Water Temperature - 70°F

Recovery- 95 - 99% depending on the reaction in water temperature

Minimum Yield - 95% recovery at optimum temperature

Safety Factor - 15%

Based on 50% of flooding velocity
Pressure drop in the column - 39 psig
or pressure drop/ft of packed tower = 6.725 psig

Flooding velocity was calculated according to the equation:

$$\frac{G_L}{G_V}\sqrt{\frac{\rho_L}{\rho_L}} \quad \text{and} \quad \frac{G_V^2 A_V \left(\mu'_L\right)^{0.2}}{g \; E \; \rho_L \; \rho_L} = 0.045$$

(Faust graph 16.4)

By the use of the above two equations the diameter can be calculated. They have the usual nomenclature as used by Faust unit operations.

Operating line

$$V^1\left(\frac{Y_1}{1-Y_1}\right) + L^1\left(\frac{X}{1-X}\right) = V^1\left(\frac{Y}{1-Y}\right) + L^1\left(\frac{X_1}{1-X_1}\right)$$

The integration was carried out by graphical method and

$$NOG = \int^{Y_2} \frac{(1-Y)\,Im}{(1-Y)(Y^*-Y)}\,dy$$

$$HOG = \frac{V}{K_y a S\,(1-Y)\,Im}$$

Height of Tower = (NOG) (HOG)

10.0 (Continued...)

10.3 (Continued...)

Pressure drop in the column was calculated as per equation:

$$\frac{\Delta \rho}{Z} = m(10^{-8}) \quad (10^{n}) \quad \frac{GL \; GV^2}{\rho_L \; \rho_L}$$

Equilibrium data for the flow conditions was found in Perry's Handbook.

10.0 (Continued....)

10.4 Pumping Calculations

$10^7$ GPD @ 50 psi

$$H.P. = \frac{10^7 \times 50 \times 2.32}{1440 \times 3960}$$

$$= \frac{116 \times 10^7}{5.7 \times 10^6}$$

$$= 203 \text{ HP}$$

203 HP = 152 KW

152 x 24 = 3660 KWH/Day

@ 1¢/KWH = 0.366¢/1000 gallons

@ 50% efficiency = 0.73¢/1000 gallon